

A. F. Yoffe



SEMI

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and*

THEIR
USE

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THEIR USE



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INTRODUCTION

First electrical engineering and then physics during the 19th century and the beginning of the 20th century were engaged in the application and study of two groups of bodies, metals (for conducting current) and dielectrics (for insulation).

During the past several decades technology has posed problems that have required new methods and new materials for their solution. There have appeared heat-resistant alloys, superhard and light alloys, plastics, organic glass, foam-glass and new building materials. The electric industry has added to its metals and insulators a group of semi-conductors.

A potential of one volt produces currents of the order of hundreds of thousands of amperes in a single cubic centimetre of metal. Under the same conditions, the current intensity in insulators is less than 10^{-7} ampere. Semi-conductors bridged the gulf between these two extremes.

A study of semi-conducting materials has shown that this quantitative difference is connected with new peculiar properties that have found diverse technical applications. An investigation of the physical nature of these technical processes has broadened the theory of semi-conductors and has elicited fresh facts that make possible the solution of many new technical problems.

A simple list of the technical problems being solved in industry through the use of semi-conductors is an indication of their importance in the economy. Semi-conductors: 1) con-

vert alternating current into direct current, 2) amplify high-frequency oscillations and generate radio waves, thereby replacing vacuum devices, 3) control current intensity and voltage, 4) protect high-voltage transmission lines from overvoltage and lightning discharges, 5) solve different problems of automation and remote control, 6) measure room temperature and intensity of illumination, 7) detect luminous and heated bodies at a distance of several dozen kilometres, 8) convert heat energy into electric energy without machines, 9) use electric current to produce cold or heat, 10) concentrate electric and magnetic energy, 11) convert sound energy into electric energy and vice versa, 12) transform ultraviolet rays into visible light and the light of one colour into that of another, 13) store light and release it on demand, 14) convert the energy of the sun's rays and of radioactive radiations into electric energy, 15) serve as sources of powerful beams of electrons in the vacuum electron devices of radio, 16) amplify weak beams of electrons millions of times, 17) act as catalysts in chemical processes, 18) serve as counters of nuclear particles.

Although this list could be continued, the number of applications named is sufficient for one to appreciate the important and diverse role of semi-conductors in modern technology.

At the same time, the study of semi-conductors has enriched physics with new ideas and laws concerning electrical phenomena; it has clarified the relation between electric charges and matter, and the nature of the forces that unite atoms and molecules into solids.

The introduction of semi-conductors into industry has only just begun, only the first steps have been taken to extend our physical conceptions on the basis of the experience gained in the study of semi-conductors. But these first steps foreshadow a future development that may change our technological patterns entirely. We may, for instance, expect that a considerable part of the steam engines, dynamos, refrigeration equipment, and possibly heating systems will be

replaced by semi-conductor thermoelements and that in radio semi-conductors will take the place of electron devices. The size and cost of such devices will then be cut dozens of times. Broad automation of all technical processes and their control from one centre will become a method easily attained in industry and will make for a deep rise in labour productivity. Daylight may be stored for lighting at night. The sun's light will produce electric power for radio receiving sets and for other household requirements. Radioactive radiations will become a source of electric power.

The special place occupied by semi-conductors in modern physics and engineering and this diversity of untapped possibilities of application is due to the peculiarities of their properties, which are not found in any other material.

We shall now make an attempt to determine these properties and to get a clear idea of their origin.

Chapter I

ELECTRICAL PROPERTIES OF SEMI-CONDUCTORS

Electrically, materials differ in their capacity to conduct electric current which is to be understood as the movement of electric charges.

In aqueous solutions or in melted salts, and also in many solid substances, the current flow is accompanied by a movement of the particles of the substance itself. Each atom or group of atoms in these substances carries the same elementary charge, whose magnitude it has been possible to measure with precision. In one second, a current of one ampere moves 6.25×10^{18} elementary charges. The quantity of electricity moved by a current of one ampere in one second is called a coulomb. Therefore, the elementary charge is equal to $\frac{1}{6.25 \times 10^{18}} = 1.6 \times 10^{-19}$ coulomb.

In metals, electric currents are not accompanied by the transfer of the atoms of the substance itself. An electric current of 10 amperes could pass from one metal into another in the course of many years without changing the composition of either metal, whereas the same current in an aqueous solution would transfer in the same period of time many kilogrammes of substance. The electric current in metals is attributed to the movement of equal size electric charges (1.6×10^{-19} coulomb) called electrons; these

charges are identical in all metals. Due to the action of light or high temperature, the electrons may break through the surface of the metal into the air or a vacuum, where it is easier to study their properties than when they are within the mass of the metal. It was found that electrons are indeed always the same, each one of them having a mass of 9×10^{-28} gm. and a negative charge of 1.6×10^{-19} coulomb.

The fact that electrons move in the body of the metal and pass from one metal into another, that electric forces direct their movement, and that electrons may leave the bounds of the metal leads to the conclusion that electrons move freely among the atoms of a metal just as gas molecules do in the air. The electrons collide with the atoms of the metal and exchange energy. It was believed that as a result of such an exchange the average energy of the electrons becomes equal to the mean energy of thermal agitation of the atoms of the metal. For this reason, the work of electric forces done during the passage of an electric current is conveyed by the electrons to the metal, which becomes heated.

This explained the liberation of heat by an electric current in a conductor.

If there is a difference of temperature in the metal, then the electrons, in passing from the hotter parts to the cooler parts, release in the cold region the higher energy obtained in the hot region. In this way, the electrons equalize the temperature inside the metal, which is the reason for the high heat conductivity of metals.

This was what was known about metals thirty years ago. Such conception, however, led to serious contradictions when compared with experiment.

The most important contradiction was connected with the thermal capacity of metals. Since electrons receive energy from and transfer energy to the atoms of the metal and increase their kinetic energy with a rise in the temperature of the metal, in much the same way as the molecules of a gas do, then by heating the metal we should expend a

rather considerable additional part of the heat in raising the energy of the electrons (one half of the heat, which goes to increase the thermal agitation of the atoms of the body). Experiment, however, shows that this is not so. The thermal capacity of a metal does not exceed appreciably the thermal capacity of an insulator containing the same number of atoms. It was found that this contradiction could not be eliminated by a partial correction of the picture just described. This became possible only as a result of a radical change in the fundamental conceptions of the structure of matter, and of the properties of all elementary particles, electrons included.

By the middle of the 1920's there had accumulated extensive experimental data which provided convincing proof that our conception of a particle as a limited minute volume filled with matter and subject to the same laws of mechanics as large bodies (for example, stones, artillery shells, or machine parts) was insufficient and one-sided. The properties of microscopic particles showed them to have wave characteristics, a thing that goes unnoticed when we deal with large bodies. Instead of forward movement along a definite path (as in the case of a thrown stone), a flow of microscopic particles (electrons or atoms) moving through matter is scattered and partially reflected; it interacts with itself becoming strong in certain directions and weak in others just as if we were dealing with the wave motion found in the propagation of light and sound. Electrons accumulate where the waves strengthen and disperse where the waves mutually weaken each other.

The conception of the atom also changed. Prior to 1925, the atom was considered to be a system that reproduced on a small scale the solar system with a heavy positively charged nucleus surrounded by negative electrons that revolved in definite orbits.

At the beginning of the 20th century, physicists believed the electron to be a minute sphere 2×10^{-13} cm. in size, with a mass of 9.1×10^{-28} gm. and a negative charge of

1.6×10^{-19} coulomb. The electron was considered the basic structural element of matter, a mere corpuscle of electric charge. Its inert mass was already at that time believed to be the result of moving electric current creating about itself a magnetic field. By accelerating the electron we increase the flow of current and strengthen the magnetic field; to accomplish this, a certain amount of work must be done, in exactly the same way as when a body of a definite mass is accelerated. According to this conception, the kinetic energy of the electron is the energy of the magnetic field surrounding it during its motion. This seemed to exhaust the properties of the electron.

At this same time (1908) V. I. Lenin, proceeding from the general principles of dialectic materialism, pointed out in his work *Materialism and Empirio-Criticism* that the electron could not be considered the ultimate structural element of the Universe and that it still concealed a limitless diversity.

Experiment has brilliantly confirmed Lenin's foresight. We already know now that in addition to charge and mass, the electron has a definite magnetic moment and angular momentum. We have learned of the existence of mesons that have the same charge (1.6×10^{-19} coulomb) and a mass (consequently also an energy) of 200, 300, 600, and 900 times that of the electron. We know that under appropriate conditions positive charges (positrons) arise that are equal in magnitude and opposite in sign to the charge of the electron and have the same mass of 9.1×10^{-28} gm.

Experiment shows that despite the tremendous number of atoms that fill the space containing a highly rarefied luminous gas, they all emit exactly the same light. The frequency of the light oscillations of a single atom is so close to the frequencies of the oscillations of all the other atoms of the same gas that the wave lengths and frequencies of the spectral lines radiated by the gas may be measured accurate to within less than a millionth part of the value being measured.

Quantum theory explains this long known but still remarkable phenomenon by the fact that each electron may exist in the atom only in very definite states of motion and may pass from one of such states (called quantum states) into another only by emitting or absorbing light of a definite frequency.

When an electron or atom is in a state of high energy it is said to be excited; when it returns to the normal state again, the electron releases its excess energy by emitting it in the form of light or by transferring it to another electron.

The quantity of released energy ϵ and the frequency ν of the emitted light are directly related to each other as follows: $\epsilon = h\nu$, where h is a factor equal in all cases to 6.62×10^{-27} erg-sec.

The factor h is known as Planck's constant.

Finally, one more important property, not only of an individual atom but also of any system of atoms, is that only one electron can exist in each quantum state. If there is an electron in one of these states, then throughout the whole system (no matter how large and complex it is) there cannot be another electron in the same quantum state.

If an atom has a large number of electrons, they are distributed in shells around the nucleus. The shell closest to the nucleus (the so-called *K*-shell) has two electrons. The next shell, the *L*-shell, is farther from the nucleus and has a total of eight electrons; in the *M*-shell there are in all 18 electrons, etc. The closer the electron is to the nucleus, the stronger it is bound to it and the greater the energy required to tear it out of the atom. The outer electrons are not so strongly bound to the nucleus and in the case of close encounter with the electrons of other atoms they are most easily influenced by the latter. The outermost electrons of different atoms may also combine, thus joining the atoms in a single system, a molecule, to produce chemical compounds. There are compounds where part of the electrons pass from one atom to another filling up the corresponding

shell in the latter. For example, when an atom of lithium (two of the three electrons of which are in the *K*-shell and only one is in the *L*-shell) comes in contact with an atom of fluorine (which has a total of nine electrons with seven of them in the outer *L*-shell), the outer electron of lithium passes over to the fluorine atom and fills up the *L*-shell to the required eight electrons. In doing so, the lithium atom, having lost one of its electrons, is converted into a positive lithium ion (with three positive charges on the nucleus and two electrons), and the fluorine atom becomes a negative ion of fluorine (10 electrons and a nucleus with nine positive charges). In the lithium ion, the *K*-shell is filled and in the fluorine ion both the *K*- and *L*-shells are filled. The bond between the ions of lithium and fluorine in the molecule of lithium fluoride is accomplished by the electrical attraction of ions of opposite charge.

A different type of chemical linkage is found in a diatomic molecule of hydrogen: the electrons of both atoms are united and situated symmetrically with respect to the two positive nuclei of hydrogen, thus joining them in a so-called valence bond.

The question now is: how do the numerous atoms (the total of which is expressed by a 22-digit number) of a solid body combine to form an entity and in what states of motion do these electrons exist?

Different types of linkage are met with in solids and in liquids, just as in molecules. In metals, for example, all atoms give up the electrons of their outermost shell and become positive ions. The totality of negative electrons, in their movement about the skeleton of positive ions, combine the latter into a strong composite of solid or liquid metal.

In crystals like diamond, the four electrons of the outer *L* shell of each carbon atom are linked up with four neighbouring atoms of carbon situated at equal distances from the atom and at equal angles. In each of the four directions, the linkage is accomplished by a pair of electrons, just as in hydrogen.

In a crystal of rock salt (sodium chloride), the atoms of sodium, which in their *M*-shells have one electron each, transfer these electrons to the chlorine atoms, in the outer shells of which there are seven electrons. Thus there appear positive ions of sodium and negative ions of chlorine. The electrostatic attraction of ions of opposite charge unites them into a cubic lattice, in which positive and negative ions alternate. This is an example of ionic linkage.

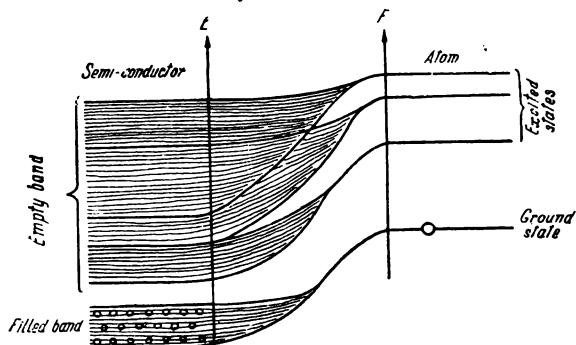


Fig. 1.

Electron energy states in an isolated atom (right) and a semi-conductor (left).

There are also other types of linkage. Thus, for example, the majority of crystals of organic substances consist of molecules uniting several atoms with strong valency and ionic bonds. On the other hand, molecules are linked together in solids by weaker forces, similar to those that manifest themselves in the collision of two molecules of gas. The electrons of both molecules do not unite into one common system but are only displaced within each molecule. Such forces of linkage are called Van der Waals' forces.

But no matter what the nature of the forces of linkage between the particles in a solid or liquid, their electrons are always governed by the following quantum laws.

When N atoms (all of the same kind) unite to form a body, then as a result of their interaction each quantum state of an electron is split up into N closely related, though distinctly different, states (see fig. 1). Only one electron can exist in each of these states.

The electron velocities, of which each individually would correspond to an electric current, compensate each other in magnitude and direction when taken as a whole, so that in the absence of an electric field no electric current is observed in the body.

Now, in an electric field the electrons moving in the direction of the electric force acting on them are accelerated, and the electrons moving in the opposite direction are retarded. Thus, the movement of electrons in the direction of the field forces predominates over that which proceeds in the opposite direction, the result being an electric current.

Taking account of the fact that only quantum states of motion are possible for electrons, we must conceive of acceleration as the transfer of an electron into a new quantum state of greater velocity, and deceleration as the transfer of an electron into a state of less velocity, and electric current as the predominance of states, that correspond to the motion of electrons from the negative pole to the positive, over the opposite states.

Let us first consider a solid or a liquid composed of N atoms or molecules that have complete outer shells of electrons, i.e., composed of particles in which all possible quantum states of the outer shells are filled with electrons. In place of each of the states of the electrons of an individual atom we will now have N quantum states of the whole body; but now also the number of electrons in the body will be N times greater than in the atom. Therefore, we should again expect all the quantum states to be filled with electrons.

The quantum properties of electrons mentioned earlier lead us to the conclusion that no electric current can be produced in such a body. Indeed, let us suppose that we

have created an electric field in the body. Despite the presence of an enormous number of electrons and the existence of a force which is exerted on each of the electrons by this field, the state of their motion will not change. To be changed, the given state must be replaced by a different state, to which there corresponds a greater or smaller velocity or a different direction of motion. But since each of the possible quantum states of motion is already occupied by some electron, no change in the state of the electron can be effected. And both before and after the electric field has appeared there will be the same number of electrons in the body moving from left to right, from right to left, up and down, and forward and backward. In other words, the total electric current of the electrons will always remain equal to zero and the body will behave as an insulator despite the tremendous number of electrons.

The situation is different if a body is made up of atoms or molecules whose outer electron shells are not filled, for example, atoms of lithium or sodium mentioned above. In the outer electron shell of each of these atoms there is only one electron, whereas the number of quantum states is two.

If a solid body is made up of N such atoms, then due to the splitting up of the quantum states, it will have $2N$ quantum states and only N electrons. The electrons that make up the solid body will occupy the N states with the least energy, and the remaining N states of greater energy will stay unoccupied. Among the occupied states there will be the same number of states corresponding to movement from left to right, from right to left, forward and backward, and up and down. For this reason, here also (just as before) there will be no electric current without an electric field. But the behaviour of the electrons in the electric field will differ sharply from that of the preceding case. There is nothing to hinder an electron, which was in a state that corresponded to motion from the negative pole to the positive pole, from passing into a new state with a greater velocity if it is free from other electrons, and this is highly

probable since the body still has an enormous number and variety of free states. This statement refers only to those electrons whose energy is already close to the energy of the free states.

Under the influence of an electric field, such an electron changes its motion in much the same way as a free electron does in a vacuum.

In actuality, the movement of an electron among the atoms of a solid (which atoms produce powerful effects on the electron by attracting, repulsing, accelerating and decelerating it) is far more complex than in a vacuum and could be taken account of only with difficulty. But the quantum theory shows that on the average the movement of an electron over a considerable number of interatomic distances does not differ from the free movement of the same charge with, however, a slightly changed mass. For this reason, we may consider such electrons free electrons capable of participating in the transfer of electric current. Such is the case in metals. And the electrons of substances that correspond to the type which we examined earlier should be considered as bound, that is, not capable of producing electric current. Such materials are insulators.

We note that the concepts "free" electron and "bound" electron have quite an unusual meaning in quantum theory. We must consider as free those electrons whose states of motion are close to the quantum states unoccupied by other electrons. The electrons whose states are adjacent only to the states already occupied by other electrons are considered bound. Thus, all the electrons making up the completely filled band of states are bound, and do not conduct electric current.

It would appear that the quantum theory leads one to the conclusion that only two types of material are possible: metals with free electrons and insulators with bound electrons.

However, we have not yet taken account of the fact that in an individual atom there are excited states of higher

energy in addition to normal states of the electron with least energy, and there even exists the possibility of an electron breaking loose from its atom altogether. If we consider a solid, not only each of its normal states, but also each of its excited states is split up into N individual states. Just as in the case when an electron of an individual atom can pass into one of the excited states by receiving the necessary energy from an outside source, so also in an insulator an electron may be transferred from the band of normal states completely filled with electrons to the band of excited states which is not occupied by any other electrons.

While the number of such electrons that have passed into the excited band is not great, they find themselves among adjacent unoccupied quantum states. Thus, as we have seen, the electrons may be considered as free and capable of participating in the passage of electric current.

Now where is the energy source to be found that will enable us to transfer electrons from the band of filled states to a "free" excited state? Such a source may be the ever-present thermal agitation of the atoms of a body. If it is intensive enough (and the work of transferring an electron to a free state is not great) then a part of the electrons will constantly be passing into the free state due to thermal agitation and the body will become a conductor of electricity. These are the substances which we call semi-conductors.

The higher the energy of thermal agitation of the atoms as compared with the energy necessary to liberate an electron, the more frequent is the transfer of electrons into the free state. However, simultaneously a portion of the excited electrons will return to the normal state, releasing the energy acquired earlier and returning it to the thermal agitation of the atoms of the body. The greater the number of free electrons that accumulate, the greater will be the number of returns to the normal state. Finally, a certain equilibrium is established in the body, and the same number of electrons is transferred by thermal agitation to the unoccupied band as is returned from there to the normal state.

In the majority of semi-conductors we have to deal with, the average energy of the atoms in the case of thermal agitation is very much less than the work required to transfer an electron to the free band. But thermal agitation is chaotic, it combines different forms of motion and all possible velocities. Even if the average energy of the atoms is not enough to liberate an electron, there are always a few atoms that have much greater velocities. The farther a given energy is from the mean value, the less the number of such cases. Thus, for example, atoms with double energy are seven times fewer than those with average energy; those with five times more energy are 140 times more rare; with 10 times more energy, 20,000 times, and with 20 times more energy, 4×10^8 times less frequent than those with average energy. Nevertheless, a certain part of the 10^{23} electrons that are found in one cubic centimetre of a body will be liberated in each of the enumerated cases.

Incidentally, if the work required to transfer an electron to a free state exceeds the average thermal energy 100 times, the number of atoms possessing sufficient thermal energy will prove much too small, in this case, only one atom in each 10^{13} . The transfer of an electron to a free state will then be an exceedingly rare exception. As a rule, the body will not have any free electrons, it will be an insulator. By way of illustration, in a crystal of rock salt the energy necessary to transfer an electron from a bound state to a free state is 200 times higher than the average energy of thermal agitation. Therefore, rock salt is an insulator.

Let us agree to measure the energy in electron-volts, as is common practice in modern atomic physics.

The charge of an electron is a strictly constant value equal to 1.6×10^{-19} coulomb. In passing through a potential difference of one volt, an electron gains kinetic energy equal to the product of its charge and the potential difference, that is, 1.6×10^{-19} joule, or 1.6×10^{-12} erg. This energy is called an electron-volt.

Expressed in these units, the average energy of thermal

agitation at room temperature amounts approximately to 0.03 electron-volt, and at other temperatures, about $10^{-4} T$, where T is absolute temperature or the temperature t in centigrade increased by 273.2° :

$$T = 273.2 + t.$$

Let us designate the energy required to transfer an electron to the free band by U electron-volts. It exceeds by $U/10^{-4} T$ times the average energy of thermal agitation of the atoms of a body. As the ratio $U/10^{-4} T$ increases, the number of free electrons in the excited states decreases.

While the energy U that is required to liberate an electron does not exceed one electron-volt, i.e., while it is not over 30 times greater than the average thermal energy (0.03 electron-volt at ordinary temperatures), the number of free electrons will be few, but still sufficient to produce measurable electric currents. However, when U is of the order of two electron-volts or more, i.e., when the work required to transfer an electron to a free state is 60 times and more above the average thermal energy of the atom, then at room temperature we have an insulator. But even in such a substance, electric conductivity may be observed at temperatures of several hundred degrees centigrade.

To liberate electrons of rock salt, an energy of six electron-volts is required, and for this reason rock salt possesses conduction electrons only at its melting point ($810^{\circ}\text{C}.$).

Thus, the difference between a semi-conductor and an insulator is one of convention: a substance that is an insulator at certain temperatures becomes a semi-conductor at other, higher temperatures. And, for example, in the case of rock salt, even if there is no electron current, at ordinary temperatures a current is conducted by sodium ions, and when near the melting point also by chlorine ions.

It is also clear that as the temperature rises the number of free electrons in each semi-conductor should increase, and, as it falls to absolute zero, the number should decrease, also to zero.

Since in a semi-conductor free electrons appear only as the result of thermal agitation, an absence of such agitation will cause the free electrons to disappear. According to this conception any semi-conductor becomes an insulator near absolute zero.

This property of semi-conductors distinguishes them from metals, in which the electrons are capable of changing their motion under the influence of electric forces and, consequently, of conducting current, irrespective and without the help of the heat energy of the atoms of the body.

Thermal agitation does not only aid in producing current in a semi-conductor by liberating its electrons, it also hinders the passage of current by impeding the free movement of the electrons.

According to quantum theory, an electric current in a semi-conductor may be described as follows.

In a perfectly built crystal, the electrons could move in nearly the same way as in a vacuum. But crystals are not perfect; accidental imperfections, impurities, and, finally, thermal agitation alter the regularity of the lattice. In approaching each other or in moving away from each other the atoms create short-lived concentrations and rarefactions.

Each imperfection in the lattice distorts the regular alternation of charges and produces a local electric field that forces the electron out of its initial path. The electron moves freely only in undistorted sections of the crystal. It is only here, over its so-called free path, that the electron accumulates energy as it increases its speed. The theory assumes that after meeting a section of imperfection in the crystal, the electron starts, as it were, from the beginning again. Each imperfection makes the electron deviate in a given direction, but there are many imperfections and they act in the most diverse directions; therefore, the sum total of their action amounts to the scattering of electrons in all directions. As a result, the action of the electric field that sends the electrons in one direction is each time upset by their

scattering during collisions with the distorted sections of the crystal (see fig. 2). The directing force of the field is felt only during transit of the free path, between collisions. This distance is very small, being of the order of a millionth part of a centimetre. For this reason an electric field is able to effect only an insignificant change in the speed of thermal agitation of the electron. However, it is only this very small, additional speed of the electrons in one and the same direction that produces electric current.

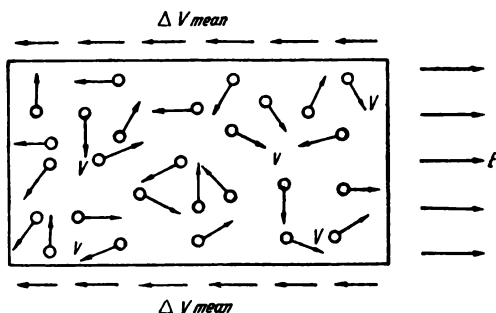


Fig. 2.

v —thermal velocities, Δv —mean additional velocity produced by the electric field E .

Even in strong electric fields, for instance 100 volts per cm., the additional energy gained over a free path of 10^{-6} cm. amounts to only 10^{-4} electron-volt, whereas the average energy of thermal agitation at room temperature is 400 times greater.

The thermal speeds of the electrons, that existed prior to the appearance of the field, are distributed throughout all possible directions; the electrons transfer just as many charges in one direction as in the opposite, thus making the sum total charge transfer along the line of the field equal to zero.

But the thermal speeds of the electrons nevertheless affect the current intensity, since they determine the free-path transit time: the higher the temperature, the greater the thermal speeds and the faster the electrons cover their free paths, the smaller also the time period between two collisions of an electron. This period is hardly at all changed by the presence of an electric field, since the field is capable of effecting only an insignificant change of electron speed. The time of free-path transit depends on the number of imperfections in the crystal lattice and on the intensity of thermal agitation.

The average additional speed imparted to the electrons by an electric field equal to one volt per cm. is called the electron mobility; we shall denote the mobility by the letter u .

In an electric field of $E \frac{\text{volts}}{\text{cm}}$, the average additional speed v_{av} will be E times greater:

$$\Delta v_{av} = uE.$$

The current intensity in a conductor may be determined as follows. Let us designate by n the number of free electrons in one cu. cm. of conductor. All electrons with a charge e that are less than a distance of Δv_{av} from a given cross section will in the course of the next second pass through the cross section; their number will be $n \Delta v_{av} S$, where S is the area of the cross section, and the charge transferred by them, or the current intensity, is

$$I = ne \Delta v_{av} S.$$

The current intensity passing through one sq. cm. of cross section, or the density of the current i is obtained by putting $S = 1$, and $\Delta v_{av} = uE$:

$$i = neuE.$$

The ratio of the density of the current i to the field E that produces it is called the specific electric conductivity σ of

the substance, and its reciprocal $\frac{1}{\sigma} = \rho$ is the specific resistance. We see that

$$\sigma = \frac{i}{E} = neu.$$

Thus, the specific electric conductivity σ of a given material is determined by the product of the concentration of n free electrons, their charge e and the mobility u . It may easily be determined by using a voltmeter to measure the potential difference at the ends of a cylindrical conductor ($V = EL$, where L is its length), and an ammeter to give the current intensity J :

$$\sigma = \frac{i}{E} = \frac{I/S}{V/L} = \frac{I}{V} \cdot \frac{L}{S}.$$

However, such measurements do not permit us to determine separately the concentration n and the mobility u of the electrons that conduct the current.

Likewise, one cannot say whether the current was caused by the movement of negative charges against the direction of the field, from the negative pole to the positive (fig. 3A), or by the transfer of positive charges to the negative pole (fig. 3B). One would, however, think the matter to be clear:

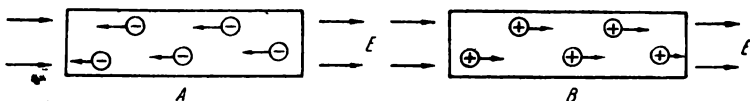


Fig. 3.

A—Current transfer by electrons; B—Current transfer by positive charges.

it is obvious that there are only negative electrons in the conductor, and absolutely no free positive charges! All the more unexpected were the results of experiments which showed that only in certain metals and semi-conductors is

current conducted by negative charges; in others, current consists in the movement of some sort of positive charges.

The sign of the current carriers may be determined by the direction of the thermoelectromotive force that originates in the conductor when one end has a higher temper-

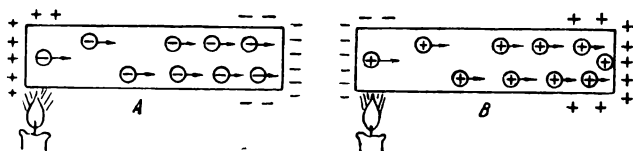


Fig. 4.

The movement of free charges to the cold end of the semi-conductor.

A—Electron current carriers; B—Positive charge current carriers.

ature than the other. At the hot end there are more free charges and their heat energy is higher than at the cold end. For this reason, the charges pass to the cold end in greater number than in the opposite direction, and charge up the cold end (see fig. 4A and 4B).

It might be expected that the cold end would become charged with negative electricity. Experiment, however, shows that both among metals and among semi-conductors there are some in which the cold end receives a negative charge (see fig. 4A) and others in which the cold end receives a positive charge (see fig. 4B).

The conclusion concerning current carriers of two signs in semi-conductors was so astounding that it was felt necessary to confirm this independently in another way. This may be done by studying the influence of a magnetic field on moving charges. As early as the twenties of last century, Ampère noticed that when an electric current passed through a flexible conductor in a magnetic field the conductor was deflected. The conductor is deflected in the direc-

tion in which the magnetic field deflects the charges moving within the conductor. If the charges are negative electrons, they move in a direction opposite to that of the current and should charge the outer, side surface of the conductor with negative electricity (fig. 5A). If, on the other hand, the charges are positive, then they move in the direction of the current and charge this side surface with positive electricity (fig. 5B). Experiments show some substances to have

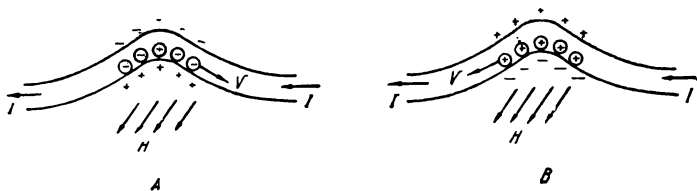


Fig. 5.

Deflection of a conductor with current I in a magnetic field H directed to the reader, perpendicularly to this drawing.

A—Electron current carriers; B—Positive charge current carriers;
V—Direction in which charges move.

positive charges and others to have negative charges. Experiments also show that the sign of the charges that are transferred from the hot end of the conductor to the cold end always coincide with the sign of the charges which are deflected by the magnetic field in this same conductor.

One has to admit that a semi-conductor is capable of sustaining the movement of free negative electrons and also that of some sort of positive charges. It is true that nuclear physics deals with positively charged positrons, but to liberate them one requires an energy exceeding one million electron-volts. They obviously do not participate in the current.

Modern quantum theory explains the transfer of current by positive charges in the following way.

We saw that when all quantum states are occupied, the electrons cannot participate in the passage of current for

the simple reason that they can change their motion only by passing into another quantum state and only into one that is free; but here there are none. However when a certain part of the electrons (even though a very small part) has left the band (they may, for example, be removed by thermal agitation of the atoms or by light), then among the occupied states there appear free places called "holes." Under the influence of an electric field, other electrons with close values of energy can pass into such unoccupied states. The electric forces retard the movement of the free negative electrons and accelerate the movement of positive charges in the direction of the field. When there are holes among the states, then electrons moving with higher speeds along the field will pass into the free states of lower speeds, which would also have taken place in the case of free electrons. But those states which were occupied by electrons are vacated, thus becoming new holes. In place of a hole corresponding to a lower speed along the direction of the field, there will appear a hole that corresponds to a higher speed. Thus, a hole changes its position in the electric field in the same way as a positive charge.

Quantum theory states that what we called positive current carriers is actually simply unoccupied states among other filled states. Incidentally, such a simple result is obtained only when the number of holes is small, i.e., when nearly all of the states are occupied by electrons.

If one speaks of holes left by electrons that have passed into excited states, then both the electrons among the free excited states and the holes among the occupied states are capable of conducting current. In such a semi-conductor, there are the same number of free electrons and free holes (see fig. 6A). An applied field will cause a current to flow. This current will be produced by carriers of both signs (see fig. 6B).

But it may happen that the holes are formed because a part of the electrons left the occupied band and became attached to impurity atoms transforming them into negative

ions (fig. 7A). Such attached electrons do not participate in the current and the only current carriers will then be the holes. This type of current is called hole current. The cold end, to which place the holes are transferred and where

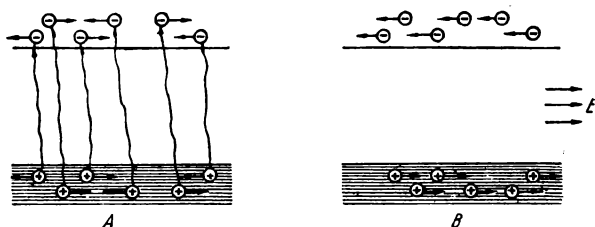


Fig. 6.

A—Formation of holes due to transition of electrons from filled band to empty band; B—Producing current in a semi-conductor by an electric field.

the deficiency of electrons is greater, becomes positively charged. In a magnetic field, the holes that carry the current are deflected to the outside thus charging this side of the semi-conductor with positive electricity.

Semi-conductors may contain impurity atoms whose electrons are loosely bound and therefore can pass into free excited states with more ease than the electrons of the basic substance; the atoms themselves become positive, fixed ions. In this case the current consists only of negative electrons, and is called "electronic" current (fig. 7B).

Semi-conductors with hole-type current are called *p*-type (positive) semi-conductors, and those of the electronic type are called *n*-type (negative) semi-conductors.

It is often sufficient to have one per cent of impurity atoms to raise the concentration of free electrons or holes millions of times. The electric conductivity of the semi-conductor is then increased the same number of times.

Thus, different impurities may be introduced into a semi conductor making it possible to control the electric conductivity within wide limits and to change the sign of the current carriers. In addition, the diversity of semi-conduct

ing materials, which include a number of elements (B, C, Si, Ge, S, Se, Te, P, As), alloys (Mg_3Sb_2 ; $ZnSb$; Mg_2Sn ;

$CdSb$; $AlSb$;

$InSb$; $GeSb$),

oxides (Al_2O_3 ; ZnO ;

UO_2 ; WO_3 ;

MoO_3),

sulphides (Cu_2S ;

Ag_2S ; ZnS ; CdS ;

HgS), selenides

and tellurides

and numerous

other more com-

plex compounds,

enables one to

select the most

suitable sub-

stance for each

concrete tech-

nical problem.

Later on we shall

see what the

reasons are for

selecting certain

materials for

given concrete

purposes.

Every year

the application

of semi-conduc-

tors in industry

is growing both

in quantity and

in diversity of forms.

We shall attempt to describe the more

important of their applications and to investigate the under-

lying physical processes.

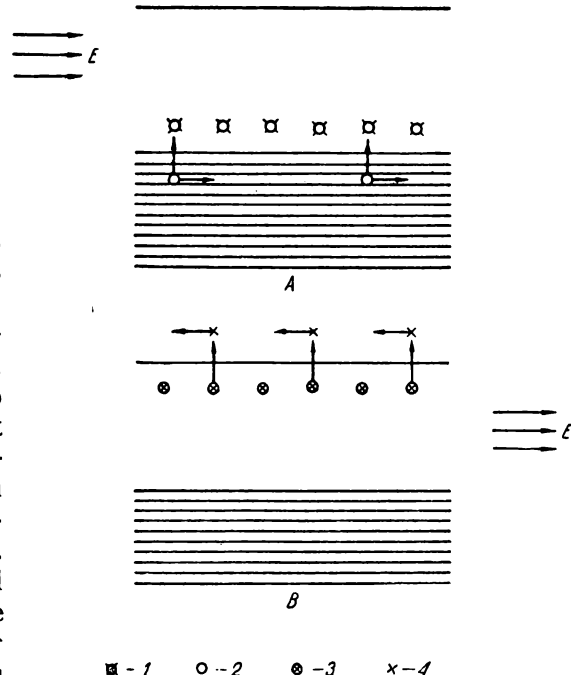


Fig. 7.

A—Formation of holes due to transition of electrons from filled band to impurity levels; B—Formation of free electrons due to their transition from impurity levels to the empty band. 1—Acceptors (receivers of electrons); 2—Free states; 3—Donors (atoms with spare electrons); 4—Free electrons; E—Intensity of electric field.

Chapter II

SEMI-CONDUCTORS IN INDUSTRY AND THE HOME

1. THERMALLY SENSITIVE RESISTORS (THERMISTORS)

Free charges are produced in a semi-conductor by the thermal agitation of its atoms. For this reason, the electric conductivity of certain semi-conductors shows a steep rise with the temperature. A temperature rise of one degree centigrade raises the electric conductivity of a semi-conductor by three to six per cent; one of 10° , approximately 75 per cent, and one of 100° increases the conductivity 50 times. By measuring the resistance of a semi-conductor one can get an idea of its temperature and, consequently, use it as a thermometer.

Such resistance thermometers, or bolometers, have been in use in laboratory work a long time for measuring very low and very high temperatures. But since metals (which vary their resistance 0.3 per cent per degree) have been used as the material of bolometers, such measurements require extreme precision. Besides, it was necessary to use a long piece of fine wire in the bolometer so that the total resistance would be sufficiently large as compared with the resistance of the lead-wires.

In this respect, semi-conductors have big advantages:
1) their specific resistance is so great that the whole bolo-

meter may be no more than several millimetres or even several tenths of a millimetre in size, and the metal lead-wires may be made as fine as required; 2) the small size radically cuts the inertia, i.e., the time required for the thermometer to take up the temperature of the medium, thus making it possible to measure the temperature of small objects that have a small specific thermal conductivity, as, for example, the leaf of a plant or the skin on the human body; 3) the relative variation of resistance of a semi-conductor is 10 to 20 times greater than that of a metal; this increases the accuracy of the measurements.

All these advantages have contributed to the broad use of semi-conductor resistance thermometers, which abroad are called thermistors. Thermistors make it possible to measure the temperature of any number of rooms or objects from a single observation post. On big ships, several thousand thermistors control the temperature at all points of interest. Thermistors are capable not only of controlling but also of maintaining a desired temperature in a given room by switching on the heater when the temperature falls and switching it off when the temperature rises too high.

The same thermistors can function in other ways, for example, they can act as time limiters. When we connect a semi-conductor resistance in an electric circuit we obtain a flow of current that increases with time. The current heats up the semi-conductor, raises its electric conductivity, and hence also the current intensity in the circuit; the semi-conductor continues to heat up, its resistance falls, and the current increases to a still greater degree. In line with the increasing temperature, the heat losses into the surrounding medium continue to grow until they equal the heat produced by the current; then an equilibrium temperature is reached, which the semi-conductor maintains as long as the given potential difference is applied to it.

The time interval required to attain equilibrium and a definite current intensity at a given potential difference is determined by the dimensions of the sample and the cooling conditions. Conditions may be selected to make this interval anything between a fraction of a second and 10 minutes.

Thermistors are used for automatic, gradual switching on of electric machines, transformers and electromagnets at given speeds. They may be used as "time relays" when an interval is required between the switching on of a given electric device and that of another.

Thermistors are also used to regulate voltage and current intensity, and to reduce accidental and systematic variations of potential differences or current intensity. To do this, a semi-conductor resistance is connected in the electric circuit together with the working part in such a way that despite any variation in the external voltage the distribution of potential in the circuit retains the same potential difference at the ends of the section in question. It then remains practically constant despite the considerable variations of voltage in the mains. Using a semi-conductor resistor it is also possible to achieve a distribution of currents such that, irrespective of any change in the line voltage, the current passing through the given device will remain constant.

Naturally, complete regulation of the current or voltage does not occur at once, but only after a certain time interval during which the semi-conductor reaches its equilibrium temperature. By selecting the proper sizes and cooling conditions, it is possible to reduce the time interval to a small fraction of a second.

In the U.S.S.R., thermistor development is due mainly to the work of Boris Timofeyevich Kolomiets.

2. PHOTOCONDUCTIVE CELLS

The energy required to transfer an electron to a free state or to form a hole may be obtained not only from thermal agitation but also from other sources, for example, the radiant energy absorbed by an electron, the energy of a flow of electrons or of nuclear particles, etc. And any increase in the number of free electrons or holes is observed in greater electric conductivity and current intensity.

The quantity of energy transferred by light to an individual electron is determined, it appears, only by the frequency of the light vibrations and does not depend on the brilliance of the ray of light. The number of light-absorbing electrons increases with the intensity of the light, but there is no increase in the energy received by each of the electrons. This surprising fact led to the idea that light waves are also a flux of particles, known as photons, the energy E of each being expressed as the product of the frequency ν of the light vibrations per second and Planck's constant h :

$$E = h\nu.$$

If the energy is measured in ergs, then h has the value of 6.62×10^{-27} erg-sec; in order to express E in electron-volts h must be taken as equal to 4.13×10^{-15} . Thus, for example, the number of vibrations of yellow light is 5×10^{14} per second; therefore, the energy of a photon of yellow light is approximately 4×10^{-15} times 5×10^{14} , or two electron-volts.

For many semi-conductors, this energy is sufficient to transfer the electrons to the free state and to raise the electric conductivity. There are also semi-conductors that require only several tenths of an electron-volt to transfer the electrons into the free state, and for this reason a rise in conductivity may be observed in the case of a much smaller frequency in the distant infrared part of the spectrum. Such radiation is produced even by very slightly heated bodies which may be detected at distances of many kilometres by

the tiny increase in current in a circuit with the proper semi-conductor. The primary, weak current rise is then amplified as many as a million times to produce the required signal.

Light is not only capable of transferring electrons to the free state inside a semi-conductor; the energy $h\nu$ imparted by the photon may prove sufficient to tear the electron from the body out into the surrounding medium. This phenomenon is known as the external photoeffect, whereas the increased electric conductivity produced by light is called the internal photoeffect, or photoconductivity, and the devices based on this effect are called photovaristors.

The materials most frequently used for photovaristors in the visible part of the spectrum are cadmium sulphide and thallic sulphide; those of infrared rays are lead sulphide, lead selenide and lead telluride.

Pyotr Ivanovich Lukirsky discovered a semi-conductor that is very sensitive to light for the external photoeffect, antimony cesium (Cs_3Sb), and Leonid Alexandrovich Kubetsky invented a semi-conductor device for multiplying the number of electrons.

Kubetsky's device (fig. 8) consists of a vacuum tube inside which are a number of plates that possess the following property: each incoming, high-energy electron produces a secondary emission (from the surface) of a larger number of slow electrons. The initial, weak flow of electrons caused by the beam of light L is accelerated by an electric field to energies of several hundreds of electron-volts, then it is bent by a magnetic field (not shown in fig. 8) and directed to the next plate, which produces a still greater number of slow electrons; they are again accelerated, then deflected by a magnet, after which they impinge on the next plate, where they again multiply, etc. If each plate increases the number of electrons two times, then 10 plates will produce an increase of 2^{10} , or 1,000 times; if the multiplying coefficient is 5, the increase will be 5^{10} times, i.e., 10^7 times. In this way, extremely weak fluxes of several electrons a second may be measured.

The external photoeffect has been used in sound motion pictures. Lately, the internal effect has found similar application. The vibrations of the sound-receiving diaphragm modulate the light ray emerging from a narrow slit and record (on moving photographic film) a strip of varying width or different degrees of blackness, in accordance with the sound

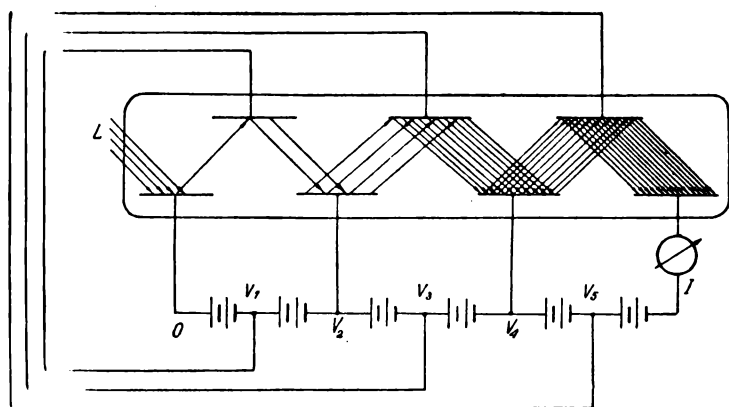


Fig. 8.

Circuit diagram of Kubetsky's device.

V_1 and V_2 are the potential differences that accelerate the electrons.

vibrations. To reproduce the sound, a ray of light is passed through the same film moving at the same speed. The quantity of light passed by the film varies in exactly the same way it did under the influence of the vibrating diaphragm during recording. The light passes through the film and falls on a photocell that produces a current proportional to the light intensity. The current then causes the diaphragm of the loud-speaker to vibrate.

Photoconductive cells are widely used for purposes of signalization and automation, and for remote control of industrial processes. They prevent accidents by automati-

cally stopping the machine when something goes wrong in the process.

For such purposes, a ray of light is directed to a photoconductive cell; a pointer placed between the source of light and its receiver indicates that the process is proceeding normally. The instant something goes wrong, the light falls on the photocell and produces a current that stops the motor.

Photoconductive cells are used to sort articles according to colour and size; the latter determines the quantity of light falling on the photocell, and hence, also the intensity of the photocurrent, depending on which the article is directed to a given section.

Photoconductive cells measure light intensity and can automatically control illumination by switching on other light sources the instant the intensity falls below the desired level.

Not only light, but also radioactive radiation, such as alpha, beta and gamma rays and fast nuclear particles (protons and deuterons) are capable of increasing the electric conductivity of semi-conductors. Each such particle produces a large number of free electrons as it passes through the semi-conductor. In some materials, for example, diamond and cadmium sulphide, the passage of one fast particle is sufficient to produce a marked current rise. Using these materials, it is possible to count the number of particles which have passed through by making the photocurrent deflect the needle of the counter one unit each time.

The study of photoelectric phenomena provides us with information concerning the properties of electrons in a semi-conductor, the energy required to transfer electrons into the free state, to liberate a hole and to tear an electron completely out of its medium.

The determination of these most important characteristics of a semi-conductor is based on a unique relation between the frequency of the light ν and the energy E conveyed by this light to the electron. We have already seen that the energy E is equal to $E = 4.13 \times 10^{-15} \nu$ electron-volts.

If E_c is the energy required to transfer an electron into the free state, then only light of a frequency at which $4.13 \times 10^{-15} \lambda > E_c$ is capable of liberating electrons and raising the conductivity. Light of a smaller frequency will prove ineffective. By determining the minimum frequency ν_{\min} of the light which is capable of producing the photoeffect, we at the same time determine the magnitude of E_c .

The energy of electrons in a semi-conductor may be judged also from a spectral analysis of the frequency of X rays that correspond to the transition of electrons to one of the states closest to the nucleus.

Spectra of X-rays fully confirmed the fact that the electrons in a semi-conductor exist either in a normal state in the filled band or in the free state. Between these two possible states there exists a region of energies inaccessible to the electron. These energies make up the forbidden band of the semi-conductor. The width of the forbidden band of energies is in different semi-conductors equal to values between several tenths of an electron-volt and one or two electron-volts.

In addition to the electrons of the crystal lattice itself, there are often (though in very much smaller numbers) electrons connected with impurities. The energies of these electrons occupy an intermediate position in the forbidden band. The impurity electrons can also participate in the photoeffect by passing into the free state.

3. THERMOCOUPLES

In 1821, Seebeck noticed that a closed circuit made up of two dissimilar metals (a thermocouple) deflects a magnetic needle situated close by each time the points of contact of the conductors have a different temperature.

The deflection of the needle was caused by the appearance of an electric current in the circuit. Curiously, Seebeck for a long time stubbornly refused to accept this explana-

tion, and considered that the phenomenon he discovered was caused by magnetization of the conductors.

A thermocouple might be regarded as a thermoelectric machine, which (without any moving parts) converts a part of the thermal energy that heats the hot junction into electric energy, the remaining part of the heat being dissipated by the cold junction into the surrounding medium. However, simultaneously a large flow of heat passes from the hot junction to the cold junction by thermal conductivity, and a certain part of the electric energy created by the thermocouple is converted into heat inside the thermocouple and cannot be utilized. This useless expenditure of heat, which the hot junction receives, is so great that the efficiency, which corresponds to the conversion of thermal energy (imparted to the hot junction) into electric energy, does not exceed 0.5 per cent for thermocouples made of metal wires. Such devices are used only for measuring temperature and are absolutely useless as technical generators of electric power.

In semi-conductors, the ratio between the electric energy produced by the thermocouple and the heat lost by thermal conductivity and liberated inside the thermocouple by current is much more favourable. Semi-conductors make it possible to put on a realistic basis the problem of obtaining electric power directly from thermal energy.

In metals, all the valence electrons are equally free at all temperatures, including absolute zero, and their kinetic energy hardly at all depends on the temperature. For this reason, the difference of temperature at the ends of a metallic conductor causes only a weak movement of charges and creates small thermoelectromotive forces of less than 10^{-5} volt per degree of temperature differences.

The situation is different in semi-conductors. The free charges here are created by thermal agitation. At absolute zero the concentration of such charges is equal to zero, and the semi-conductor becomes an insulator. As the temperature rises, the increase in the concentration of free electrons or

holes is exceedingly rapid, attaining at room temperature from 10^{15} to 10^{20} .

The kinetic energy of a free electron in a semi-conductor (as distinguished from a metal) does not remain constant, but varies in direct proportion to the absolute temperature (i.e., the temperature measured from absolute zero).

For this reason, a difference of temperature in a semi-conductor causes a movement of free charges.

If the current carriers are electrons, they convey their charges to the cold end making it negative, whereas the hot end of the semi-conductor that has lost a part of its electrons becomes positive. This produces a difference of potential between the hot and cold ends. On the other hand, in a *p* type semi-conductor the hot end becomes negative and the cold end positive.

If the semi-conductor is insulated, then the increase of the potential difference within the semi-conductor produces a proportionate increase in the electric field which retards the flow of electrons from the hot end to the cold end and accelerates the flow in the opposite direction. After a certain time lapse the potential difference between the hot and cold ends becomes such that the flow in both directions is equal. It is this equilibrium that determines the thermoelectromotive force, which is dozens of times greater than in metals, reaching or even exceeding 10^{-3} volt per degree of temperature difference. If a semi-conductor with a temperature difference is part of a closed electric circuit, then the flow of charges does not cease and creates a current in the circuit, thus generating electric energy. There are special advantages to a device that uses both *p*-type and *n*-type semi-conductors since their currents are in the same direction and therefore strengthen each other.

The quantitative difference between a semi-conductor and a metal produces new qualitative possibilities. The efficiency of semi-conductor thermocouples reaches seven per cent but may be even greater. Of the heat engines now in use, only the internal combustion engine that requires high-quality

liquid fuel, such as petrol, kerosene and oil, has an efficiency of the order of 40 to 50 per cent. The efficiency of the best steam power stations hardly reaches 30 per cent, while that of low-power steam engines is 10 per cent; locomotives consume fuel with an efficiency of four to eight per cent. If we take into consideration the extreme simplicity of thermoelectric generators which do not require either the complex rotating parts of heat engines, or dynamos, and also the small size and stable operation of thermocouples, it may be expected that semi-conductor thermopiles will occupy a place of no small importance in the power output of the country. It is also possible that thermocouples will open the way to the utilization of new sources of heat wherever there are considerable temperature differences. It will probably be possible to convert the energy of the sun's rays into electric power through the use of thermopiles.

In the Soviet Union thermocouples were first put to practical use to supply with radio regions that had no electricity. Here the source of heat is the hot gases emerging from the glass chimney of a kerosene lamp; they pass inside a vertical tube placed over the chimney and heat the inside junctions of the thermocouples arranged radially about the tube.

The outside junctions are air-cooled and are connected to radiator-type metal plates to improve cooling. In this device, the inside junctions are heated to 300° - 350° , whereas the temperature of the outside ones does not exceed 60° . The temperature difference of 250° to 300° that is maintained by the kerosene lamp is sufficient to produce the electric energy required to feed a radio receiving set. The thermopile consists of two parts: one part supplies filament current for the valves and the other produces a voltage of about 100 volts for the plate circuit. Experience has shown that such thermoelectric generators developed by the Institute of Semi-Conductors of the U.S.S.R. Academy of Sciences (A. F. Yoffe, Y. P. Maslakovets, A. N. Voronin and others) in cooperation with the Ministry of Communications of the U.S.S.R. (V. S.

Daniel-Bek and others) produce sufficient electricity for radio-receiving sets. They are now in production. A thermopile of this type is shown in fig. 9.

More powerful thermoelectric generators heated by kerosene stoves supply electricity to "Urozhai" type radio stations used in machine-and-tractor stations.

The problem of supplying outlying districts with radio will be simplified still more when glowing-cathode vacuum tubes are replaced in radio sets by semi-conductor devices and amplifiers that require no heating and therefore still less electricity. The whole outfit will then be more compact, and the economized energy of the thermopile may be used for a series of loud-speakers connected to the receiver, especially if the latter are provided with semi-conductor sound generators that consume hardly any power at all.

Naturally, thermoelectric generators are not limited to one definite fuel, say, kerosene; it is just as simple to con-

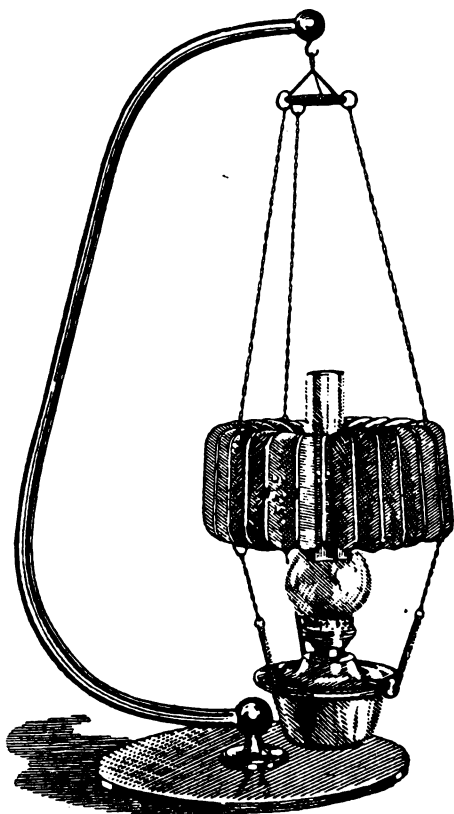


Fig. 9.

Type TGK-3 thermoelectric generator.

struct them for use with coal, wood, peat or any other fuel.

Let us consider the design of a semi-conductor thermocouple and thermopile for the generation of electric power.

The thermocouple shown in fig. 10 consists of two semi-conducting branches connected by a metal wire; one of the branches is made of n -type material and the other of p -type material. The metal bridge R_0 connecting them is heated from some source. The other two ends, which are cooled

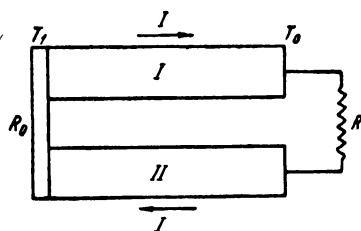


Fig. 10.

Thermoelectric circuit.

by air or running water, are connected to the external circuit that utilizes the electricity produced by the thermocouple. In our case, the external circuit is a radio set. In other cases it may be an incandescent or fluorescent lamp if lighting is required, or an electric motor, if mechanical energy is desired, etc.

This is explained in fig. 10, where I and II denote the two branches of the thermocouple which consist of semi-conductor rods; R is the electric resistance of the consumer of electric power. Let us assume that branch I is an n -type semi-conductor, and branch II is a p -type semi-conductor. Then the electric field, and hence also the electric current, will be directed as indicated by the arrows; in branch I, from the hot end to the cold end, and in branch II, from the cold end to the hot end, thus combining in a counterclockwise direction (the direction of the field and of the current is considered as being from the positive pole to the negative, that is, in the direction in which the positive charges move).

We shall designate the absolute temperature of the hot ends of the thermocouple by T_1 and the cold ends by T_0 . If α_I and α_{II} denote the thermoelectromotive forces that ap-

pear in branches I and II due to a temperature difference of 1°C . between the ends, the total e.m.f. E , that corresponds to the temperature difference $(T_1 - T_0)$ will be:

$$E = (\alpha_I + \alpha_{II}) (T_1 - T_0).$$

The current I which will flow in the closed circuit made up of the internal resistance R_0 of the branches of the thermocouple and the external resistance R of the consumer, will be equal to:

$$I = \frac{E}{R + R_0}.$$

The useful power W obtained by the consumer may be expressed as:

$$W = V \cdot I,$$

where V is the difference of potential at the ends of the external resistance R . Since in a direct current circuit (which is what we are dealing with) the potential drop is directly proportional to the resistance, then

$$\frac{V}{E} = \frac{R}{R + R_0}, \quad V = \frac{ER}{R + R_0}$$

and

$$W = \frac{E^2 R}{(R + R_0)^2}.$$

By substituting in place of E its value we obtain a general expression for the useful power W produced by the thermocouple:

$$W = (\alpha_I + \alpha_{II})^2 (T_1 - T_0)^2 \cdot \frac{R}{(R + R_0)^2}.$$

W reaches a maximum when $R = R_0$; the maximum power that a thermocouple is capable of producing for an external consumer is equal to:

$$W_{\max} = \frac{(\alpha_I + \alpha_{II})^2 (T_1 - T_0)^2}{4R}.$$

And the total electric power developed by a thermocouple is:

$$EI = \frac{(\alpha_I + \alpha_{II})^2 (T_1 - T_0)^2}{2R}.$$

In order to maintain the difference of temperature, it is necessary continuously to transmit thermal energy to the hot junction and dissipate the heat from the cold ends. A large part of the heat supplied to the thermocouple disappears to the cold ends by reason of thermal conductivity of the branches. Part of the electric energy produced by the thermocouple is lost in heating the branches. These irreversible processes reduce the efficiency of the device drastically. If it were possible to avoid such processes completely (but this is impossible since every semi-conductor possesses thermal conductivity and electric resistance), a thermocouple would give the highest efficiency η of any reversible machine that is possible according to the laws of thermodynamics:

$$\eta_{\max} = \frac{T_1 - T_0}{T_1}.$$

In the case of a thermopile for radio reception, T_1 may be taken equal to $350^\circ + 273^\circ = 623^\circ$ and $T_0 = 50^\circ + 273^\circ = 323^\circ$, whence

$$\eta_{\max} = \frac{623 - 323}{623} = 0.48 = 48\%.$$

In actuality, however, the efficiency η of a thermopile comes to only a few per cent. This example shows what a tremendous role is played by the processes of thermal conductivity and the generation of joulean heat by current.

If we want to obtain greater efficiency η , and not maximum power W , the ratio between the external resistance R and the internal resistance R_0 should be different, R should be greater than R_0 . In this case, of the total power EI pro-

duced by the thermocouple, use is made of over half of the power W . An analysis of the processes that take place in the thermocouple shows that the sharp cut in the efficiency (it is a reduction of a large number of times as compared to the thermodynamically possible value η_{\max}) is caused principally by the irreversible process of heat conductivity.

Let us therefore examine the problem of heat conduction within semi-conductors. Here, temperature levelling takes place in two ways simultaneously. Heat is transferred: 1) by the electrons and 2) by the thermal agitation of the atoms. The electrons of the hot end have a higher kinetic energy and pass to the cold end where they release to the atoms their excess energy, thus increasing the thermal agitation of the atoms and also the temperature. The electrons of the cold end have less kinetic energy, so in passing to the hot end they reduce the thermal agitation and the temperature. And since the same electrons also conduct electric current in the semi-conductor, the transfer of heat and the conduction of current are closely related processes.

The thermal conductivity of a material is characterized by a certain coefficient κ which may be defined as follows. If we take a cylindrical rod of a given substance with a cross section of one sq. cm., in which the temperature varies one degree per centimetre of length, then in the direction from hot end to cold end κ calories of heat will be transferred in one second.

If the cross section area of the rod is S cm.², its length L cm. and the temperature difference on its ends ΔT° , then by reason of thermal conductivity \dot{Q} calories will pass from the hot end to the cold end in t seconds:

$$Q = \kappa \frac{\Delta T}{L} S t.$$

The coefficient of thermal conductivity may be expressed either in cal/sec. \times deg. \times cm., or in watt/deg. \times cm. Since 1 cal./sec. corresponds to 4.19 watts, the numerical value

of κ expressed in watts is 4.19 times that expressed in cal./sec.

On the other hand, the electric current produced in this substance by the same electrons is determined by the specific electric conductivity σ of the substance. In the same type of rod of length L and cross section S and potential difference ΔV between its ends, a quantity of electricity q ($q = \sigma \frac{\Delta V}{L} St$) will pass between its ends in t seconds.

The relation between thermal conductivity κ and electric conductivity σ for various metals was found by Wiedemann and Franz who used purely empirical methods. Experiment showed that:

$$\frac{\kappa}{\sigma} = A_m T,$$

where T is the absolute temperature and A_m is a constant for all metals.

The quantum theory of semi-conductors likewise leads to the relation $\frac{\kappa}{\sigma} = A_s T$, however, the coefficient A_s has a different meaning.

This relation between κ and σ makes it absolutely impossible in principle to produce a reversible thermocouple. To eliminate the thermal conductivity, it is necessary that $\kappa = 0$; in order to eliminate joulean heat losses it is necessary that the resistance of the branches of the thermocouple should equal zero, and the reciprocal of σ infinity. But the demand that $\kappa = 0$ and $\sigma \infty$ at one and the same time is incompatible with the Wiedemann-Franz law.

Let us now consider the second type of thermal conductivity. Thermal conductivity in semi-conductors is accomplished not only by electrons but also through the thermal agitation of the atoms of the crystal lattice. The mechanism of this process may be explained as follows. The random thermal movements of the atoms of a solid may be regarded as the sum total of their different vibrations, which include

the mutual vibrations of individual atoms, the vibrations of pairs, of groups of three, etc., right up to the vibrations of the body as a whole. The higher the temperature, the more intensive the vibrations.

Each of these numerous vibrations propagates in the body as an elastic wave transferring its energy.

Thus, the coefficient of thermal conductivity κ of a semi-conductor consists of two parts: the thermal conductivity κ_{el} due to the electrons and the thermal conductivity κ_{th} created by the thermal agitation of the atoms of the body. The value of κ_{el} is directly proportional to the specific electric conductivity σ .

Therefore, when the concentration of free electrons in a semi-conductor varies, the coefficient κ_{el} varies in direct proportion to σ , whereas κ_{th} remains nearly constant. The total thermal conductivity κ may be expressed as:

$$\kappa = A_s T \sigma + \kappa_{th}.$$

And our experiments confirmed this dependence of κ on σ .

The coefficients of thermal conductivity κ_I and κ_{II} of the branches of the thermocouple play an important part in determining its efficiency; in addition, of considerable importance are the thermoelectromotive forces α_I and α_{II} and the specific resistances ρ_I and ρ_{II} of both branches. Calculations show that given the temperatures of the hot end T_1 and the cold end T_0 , the efficiency of the thermocouple is determined by one value z , which depends on the enumerated characteristics of the materials of the thermocouple:

$$z = \frac{(\alpha_I + \alpha_{II})^2}{(\sqrt{\kappa_I \rho_I} + \sqrt{\kappa_{II} \rho_{II}})^2}.$$

The greater z is, the higher the efficiency; and for a given z the efficiency is always the same, irrespective of the individual values of α , κ and ρ . Calculations show that the

efficiency does not depend on the size and form of the branches, but only on T_1 , T_0 and z . The efficiency of a thermocouple may be expressed as follows:

$$\eta = \frac{T_1 - T_0}{T_1} \frac{\sqrt{1 + \frac{1}{2} (T_1 + T_0) z - 1}}{\sqrt{1 + \frac{1}{2} (T_1 + T_0) z + \frac{T_0}{T_1}}}.$$

For metals, z has values of the order of several units multiplied by 10^{-5} , for semi-conductors 10^{-3} and higher, that is, several dozen times more. In accordance with these values of z , the efficiency of semi-conductor thermocouples is also dozens of times higher than that of metallic thermocouples.

If one wishes to obtain considerable voltages, a large number of thermocouples are connected in series, forming a thermopile. Thus, given a thermoelectromotive force of $\alpha_I + \alpha_{II} = 4 \times 10^{-4} \frac{\text{v}}{\text{deg}}$ and a temperature difference of $T_1 - T_0 = 300^\circ$, the electromotive force of an element $E = 4 \times 10^{-4} \times 300 = 0.12$ volt. In order to obtain an electromotive force of 120 volts, 1,000 such elements must be connected in series. If it is desired to obtain strong currents, the elements are connected in parallel. The greater the quantity of heat Q that passes through each square centimetre of hot junction, the smaller the size of the thermopile required to generate the given electric energy.

The above considerations determine the desired design of the thermopile, the efficiency of which does not depend on its form or on the method of connecting its elements.

4. REFRIGERATORS

Soon after Seebeck's discovery, Peltier, in 1834, observed a phenomenon that proved to be closely connected with thermoelectricity. Incidentally, Peltier himself did not suspect this. He wanted to prove that the heating of conductors by weak currents does not conform to the general law of

Joule and Lenz for conductors and exhibits individual peculiarities in different metals. To do this, he built circuits made up of different metals. Although the measurements of the heat generated in them by the current did not justify Peltier's expectations, he did notice and describe strange heat effects at the junctions of two different metals. In 1838, Academician Lenz of St. Petersburg showed in a beautiful experiment that at the point of contact of different conductors electric current either releases or absorbs a definite quantity of heat. Lenz placed a drop of water on the joint of two metals and froze it by passing a current.

We now know that the quantity of heat Q produced or absorbed at the junction of two conductors is proportional to the current intensity I and the absolute temperature T of the joint of the conductors:

$$Q = AIT.$$

Coefficient A is equal to the sum of the thermoelectromotive forces $\alpha_I + \alpha_{II}$ of the branches of the thermocouple. The sign of the value Q (i.e., the receipt or loss of heat at the joint) depends on the sign of I , i.e., on the direction of the current.

The current which we examined earlier and which arises in the closed circuit of a thermocouple cools the hot junction and warms the cold junction. If by using an external source we pass a current through a thermocouple in the reverse direction, it will liberate heat on the hot junction and absorb heat from the cold junction. One and the same junction of two conductors heats up when the current is in one direction and is cooled when it is in the opposite direction.

Calculations show that the temperature difference, which can be produced in this way, and also the quantity of heat which the current removes from a given junction and imparts to the other junction is determined by the same value A as the efficiency of the thermocouple.

The same properties of the material of both branches de-

terminated by the values α , κ and ρ characterize the production of electric energy in a thermoelectric generator and the cooling process in a refrigerator.

By maintaining the temperature of the heated junction close to room temperature and by constantly dissipating into the surrounding air the heat generated here, it is possible to cool substantially the other junction and through it, the surrounding air. Thus, using semi-conductors with a large enough value of z , it is possible to obtain low temperatures in a refrigerator. Domestic refrigerators may be designed to operate on this principle (see fig. 11).

On the other hand, the Peltier effect may be applied to heat the rooms in a building or to warm up food. Such problems have long been solved in a simpler way, by the generation of joulean heat in a rheostat or an electric range. In this case, the quantity of thermal energy produced is equal to the electric energy expended.

The thermoelectric system of heating a room differs essentially from the action of an electric range. By passing an electric current through a thermoelectric circuit, we not only heat the whole conductor as usual, we also cool one junction and heat the other. A certain quantity of thermal energy Q_0 is removed from the junction being cooled and may be expressed as follows:

$$Q_0 = \alpha \cdot T_0 \cdot I \cdot t,$$

where α is the thermoelectromotive force, T_0 is the absolute temperature of the cold junction, I is the current intensity and t is the duration of the current in seconds.

Accordingly, the warm junction (the absolute temperature of which we shall denote by T_1) dissipates a thermal energy Q_1 :

$$Q_1 = \alpha \cdot T_1 \cdot I \cdot t$$

which is greater than the heat Q_0 in the ratio:

$$\frac{Q_1}{Q_0} = \frac{T_1}{T_0}.$$

If we confine ourselves to a consideration of the processes on both junctions, the following description may be given. The electric current removes from the cold junction a quantity of heat Q_0 and transmits to the warm junction a greater quantity of heat Q_1 , by supplementing the deficient energy $Q_1 - Q_0$ in the form of electric energy W .

The energy W is added to the heat Q_0 removed from the cold junction, and their sum $Q_0 + W = Q_1$ is released on the warm junction.

From the data concerning the values of Q_0 and Q_1 it may be seen that the ratio of electric energy expended W to the heat Q_1 that is liberated on the warm junction, is equal to:

$$\frac{W}{Q_1} = \frac{Q_1 - Q_0}{Q_1} = \frac{T_1 - T_0}{T_1}.$$

If, for example, the absolute temperature of the warm junction is $T_1 = 300^\circ$, which corresponds to $+27^\circ\text{C.}$, and the temperature of $T_0 = 270^\circ$, or -3°C. , then:

$$\frac{W}{Q_1} = \frac{30}{300} = 0.1.$$

In other words, in order to transfer 100 calories of heat into a warm room at a temperature of 27°C. , one might use

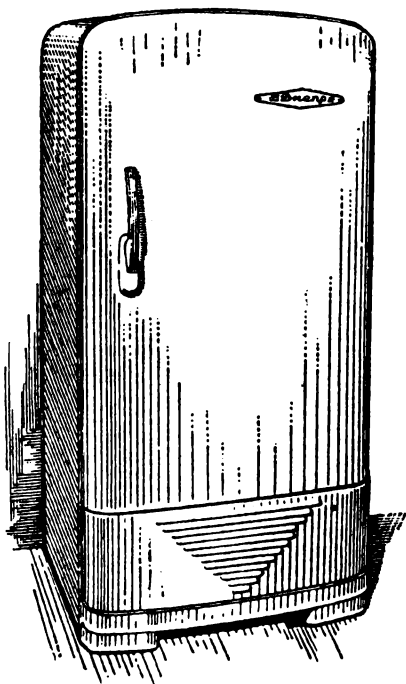


Fig. 11.
Thermoelectric refrigerator.

90 calories taken from a cold medium (the air, for instance) and add only 10 calories of electric energy.

Since it is very easy to take 90 calories from the surrounding cold air or from a water reservoir, we have the intriguing possibility of expending only 10 calories of electric energy and thereby conveying to the warmer room 100 calories of heat.

Unfortunately, the actual process in a thermopile is not limited to the releasing and absorbing of heat at the junctions. A current of heat arises along the branches of the thermopile itself from the warm junction to the cold junction; this opposes the transfer of heat (which accompanies the current flow) in the opposite direction. In addition, a part of the electric energy of the current is converted into heat in both branches of the thermocouple.

Due to these two processes, the utilization of electric energy is sharply increased, requiring not a 10 per cent boost in electric energy but one of approximately 60 per cent. But even this result is of considerable interest: the expenditure of electric energy amounts only to about one half of the heat entering the room, the remainder being supplied by the cooler outside air or by running water at temperatures close to zero.

The smaller the difference $T_1 - T_0$ as compared with T_1 , the more efficient is the thermopile as compared with an electric heater of the resistance type.

The thermopile has another important advantage. If the direction of the current is reversed, Q_0 heat will begin to generate on the outside junctions, while the junctions that had been heating the room will absorb the heat Q_1 , and in this way will cool the room. The same thermopile can cool the air in summer. By regulating the intensity and direction of the current in the pile, it is possible to maintain a given temperature in the room, irrespective of the temperature of the outside air.

As we have already seen, the cooling effect produced by a thermopile may be used for purposes of refrigeration. The

warm junctions give up (to the surrounding air or to the house water) the heat Q_1 , which they receive, while the cold junctions inside the refrigerator absorb heat, thus maintaining any desired low temperature.

Modern engineering has produced different types of refrigeration equipment. The fewer irreversible processes such machines have, the higher their efficiency and the closer it is to the thermodynamical efficiency. Complex refrigerators with a higher efficiency than the thermopile type exist, but the latter have the advantage of simplicity and absence of moving parts.

5. SEMI-CONDUCTOR FERROMAGNETIC MATERIALS (FERRITES)

The peculiar magnetic properties of iron, cobalt and nickel, or the ferromagnetic metals (the name comes from the first of these elements, iron, the Latin for which is *fer-um*), are to be explained by the fact that in them large groups of atoms (so-called domains) have magnetic moments of the same direction. The effect of a magnetic field on ferromagnetic materials is different from the effect of such a field on other metals, where the random thermal agitation is made up only of individual atoms, whose energy even in a strong magnetic field is able to change only by a magnitude of the order of 10^{-16} erg, or 10^{-4} electron-volt. In ferromagnetics large groups of millions of atoms participate in the thermal agitation and their energy in a magnetic field may increase or decrease by several electron-volts, depending on the direction of the field. In the absence of a magnetic field, the moments of the atoms or domains are scattered in all directions by the thermal agitation.

The magnetic field tends to align the magnetic moments with the direction of the field, while the thermal agitation continues to scatter them in all directions. The average energy of thermal agitation at room temperature amounts

to approximately 0.03 electron-volt, and so it easily overcomes the magnetizing force of a field acting on the individual atoms of ordinary (non-ferromagnetic) bodies. The only thing retained is the slight predominance of atoms whose magnetic moments are along the direction of the field. The additional magnetization produced by these atoms changes the magnetic field by a millionth part.

The situation is just the reverse in ferromagnetic metals, where the energy change, created by the magnetic field when a whole domain turns about, exceeds that of thermal agitation; here, therefore, the orienting effect of the magnetic field is predominant and magnetization of the ferromagnetic increases by hundreds and thousands of times the magnetic effects of the external field. Higher temperatures increase the thermal agitation, thus reducing the orienting action of the magnetic field. The French scientist Curie showed that for each ferromagnetic material there exists a critical temperature (the Curie point) above which the domains break down and the metal loses its ferromagnetic properties. For iron, the Curie point is $780^{\circ}\text{C}.$, for nickel $360^{\circ}\text{C}.$

Ferromagnetics, as iron for instance, are widely used in electrical engineering, where powerful magnetic fields are required. Iron is used in the manufacture of cores for alternating current transformers, of the bodies and rotors of electric machines, and electromagnets.

One of the drawbacks to using ferromagnetic materials in alternating current circuits is the energy losses that produce heating. These losses are caused 1) by retarded turning of domains (hysteresis) and 2) by strong induced currents arising from constant variations of the magnetic field in alternating current conditions, and they increase with the frequency of the current and the electric conductivity of the material.

To reduce the induced (Foucault) currents, the iron is made in the form of insulated laminations and is used as powder distributed in an insulating material. Nevertheless, Foucault currents limit the use of iron in the case of high

frequency alternating currents. There is no purpose in using iron for radio frequencies since it practically does not change the magnetization.

For this reason, ferromagnetics which have a high specific resistance and produce only weak induced currents in high-frequency fields and cause small losses of energy, should be of great importance.

In recent years, semi-conducting materials have yielded a rather large group of materials similar in structure to the mineral spinel. They are compounds of the oxides of a trivalent metal (trivalent iron or aluminium, for example) and a bivalent metal such as zinc. These semi-conductors proved to be ferromagnetics with extremely high magnetic properties and at the same time a large specific resistance. They were given the name ferrite. A large number of different ferrites have been made and their quality is being constantly improved. Ferrites make possible high magnetizations at frequencies of a million and more cycles per second.

In addition to ferromagnetic materials in which the magnetic moments of all the atoms of a single domain are parallel to each other, there are substances, including semi-conductors, where the atoms and their electrons in each domain have pairs of equal but oppositely directed magnetic moments. Such substances are called anti-ferromagnetics. Just as in the case of ferromagnetic materials, they have a definite temperature (the Curie point) at which the special structure of the domain breaks down and the anti-ferromagnetic material loses its specific properties.

But whereas in ferromagnetics, the passing of the Curie point signifies a sharp reduction of magnetic properties, in anti ferromagnetics the magnetic properties improve above the Curie point; the magnetic moments below the Curie point mutually cancel in pairs and the total magnetic moment of the body is close to zero.

Ferrites have opened up the possibilities of concentrating, in a small space, considerable magnetic energy not only in

direct current conditions and in the case of low-frequency alternating currents, but also at high frequencies in high-frequency transformers with ferrite cores, thus sharply reducing the size of many radio devices.

The growing diversity of ferromagnetics with different properties has put into the hands of the experimenter and engineer a broad range of materials to choose from for the best solution of the problems that confront them. The appearance of semi-conducting ferrites is a big step forward in electrical engineering and especially radio.

6. SEIGNETTE-ELECTRICS AND PIEZOELECTRICS

In the 1930's, Igor Vasilyevich Kurchatov and Pavel Pavlovich Kobeko made a comprehensive study in seignette salt (Rochelle salt) of a phenomenon which in the field of electricity bears a close analogy to that of ferromagnetism in the magnetic field. They called this phenomenon seignette-electricity from the name of the principal representative of such substances. It is also called ferroelectricity.

Just as ferromagnetics have regions with aligned magnetic moments, so also in seignette-electrics there are large regions characterized by alignment of the electric moments. For this reason, the electric field turns the whole of such a region in the direction of the field and overcomes the thermal agitation that tends to scatter the electric dipoles in different directions. The aligned electric fields of such regions of a seignette-electric combine with the external electric field, increasing it by thousands and tens of thousands of times. The charge of a condenser is increased the same number of times when a seignette-electric is used in place of air. And the electric interaction of charges in this field is reduced the same number of times. The number which shows how many times the above effects of an electric field change

when filled with a given substance is called the dielectric constant of this substance.

Whereas the dielectric constant of ordinary insulating materials is measured in units or tens, in seignette-electrics it is of the order of several thousand.

The lower the temperature and the stronger the electric field, the more predominant is the effect of the latter over the random thermal agitation. In sufficiently strong fields, the electric dipoles of all regions of the seignette-electric are practically in the direction of the field. This produces the greatest possible electrization. A similar phenomenon of saturation of the magnetic properties is also observed in ferromagnetic materials.

Both seignette-electrics and ferromagnetics have a Curie point above which the formation of domains is disrupted by thermal agitation, and the dielectric constant is reduced to the usual small value. The Curie point for Rochelle salt was found to be 24°C.

Kurchatov and Kobeko observed that Rochelle salt (as distinguished from ferromagnetics) has a so-called lower Curie point below which the domains are fixed in position to such an extent that they are not able to change the direction of their electric moments under the influence of an external electric field, and therefore the dielectric constant is small.

Other phenomena are observed in Rochelle salt that are peculiar to ferromagnetics; for example, hysteresis, i.e., a lag in electrization variations as compared with changes in the electric field. When the field increases, the electrization is less than that which should correspond to the given field. As the field decreases, the electrization does not decrease as much as would be expected; it retains a rather high value. When the field falls to zero, electrization is retained. This is residual electrization, similar to the residual magnetization of ferromagnetics which makes it possible to produce permanent magnets.

Rochelle salt has to be grown in the form of single crystals.

tals, which, however, are very hygroscopic and already at 24°C. lose their exceptional properties. That is why the discovery of similar properties in barium titanate (TiO_3Ba) by Bentsion Moiseyevich Wul was an important event.

Barium titanate is a firm ceramic mass readily prepared and easily made into any form by pressing and roasting. Its Curie point lies above 100°C. Wul's discovery is of great importance in the manufacture of condensers, especially for radio, because the dielectric properties of barium titanate are excellent and the raw materials are cheap.

Condensers made of barium titanate and similar materials concentrate considerable quantities of electric energy within a small space in much the same way as ferrites concentrate magnetic energy.

Georgi Anatolyevich Smolensky added some more seignette-electrics and ferrites to those already known.

Thus, the electric and radio industry has added to its metal ferromagnetic material and its dielectrics made of organic insulators and mica, an extensive and rapidly growing assortment of semi-conductors, which make for a better solution of technical problems, including those that could not be solved by existing materials, as, for example, the manufacture of cores for radio transformers or nonlinear condensers mentioned above. The introduction of seignette-electrics and ferrites has greatly reduced the size of many devices, and especially radio parts.

If we also take into account the new possibility of replacing vacuum radio valves with tiny 2-mm. semi-conductor detectors and amplifiers, and also the possibility of using thermopiles to supply radio equipment with electricity, the extent of the revolution that is being made in the radio industry by semi-conductors and the new conveniences of radio in the home will be clear.

In addition to its excellent dielectric properties, Rochelle salt exhibits very marked piezoelectric properties. This phenomenon is also peculiar to other crystals, for example quartz, and consists in their electrization through elastic

deformation. Due to compression or tension, charges of opposite sign appear on the opposite faces of a crystal.

The piezoelectric properties of these crystals are to be explained by the presence within them of electric dipoles situated in definite crystallographic directions. In the case of compression, the dipoles approach one another and their total electric moment changes, which is the reason for the appearance of charges on the surface of the crystal or on the adjacent electrode. In the case of tension, the charges on the plates reverse their sign.

When a potential difference is applied to the plates of a piezoelectric, the electric field produces compression or tension of the crystal by bringing together or by separating the dipoles. Compression is created by the same difference of potential which appeared during tension, and tension is caused by the electric field that appeared during compression of the crystal.

Compression or tension imparts elastic energy to the crystal; within the piezoelectric, a part of this energy passes into the energy of the electric field. And, conversely, the application of an electric field causes a corresponding elastic deformation.

Thus, what takes place in a piezoelectric is the conversion of elastic energy into electric energy and vice versa. The efficiency of each of these processes is close to 100 per cent since irreversible phenomena are nearly absent.

If a rapidly alternating electric field is applied to a piezoelectric and if the frequency selected is such that it coincides with the frequency of the vibrations of the crystal or of one of its harmonics (for example, the vibrations of halves, thirds, or fourths of that of the crystal), the crystal will begin to vibrate intensively at this resonance frequency. The alternating potential difference will cause a periodic compression and tension, which in their turn will create corresponding charges and a corresponding varying potential difference. In this way, continuous oscillations will be set up in the crystal.

The frequencies of such oscillations may be very great. Indeed, resonance sets in when the sound wave is reflected from both external surfaces and is converted into a standing wave with nodes at the ends, i.e., when the thickness of the crystal is equal to one half the wave length, λ , which is expressed as the quotient of the velocity of sound v (the distance covered by sound vibrations in one second) by the frequency ν (i.e., the number of waves emerging from the source in one second): $\lambda = \frac{v}{\nu}$; $\nu = \frac{v}{\lambda}$

The velocity of sound v is a magnitude of the order of 3×10^5 cm. per sec; if $\lambda = 1$ cm., then ν will equal 3×10^5 sec⁻¹. Elastic vibrations of such a frequency are not detected by the ear and are known as ultrasound.

Thus, piezoelectrics serve as a source of ultrasonic waves. At sea they are used to measure depth, the distance to shore, the position of icebergs, submarines, shoals of fish, and the like. High-frequency electric currents produce the energy for ultrasound. In the piezoelectric they transform their electric energy into elastic energy, and then into the acoustic energy of ultrasound in the surrounding medium.

The same piezoelectrics serve as receptors of ultrasound which produces elastic vibrations in the crystal; the elastic deformations of the crystal are converted into electric oscillations that are detected by instruments.

Anatoly Vasilyevich Rzhakov and B. M. Wul investigated the piezoelectric properties of barium titanate that had been electrified by an electric field. On the basis of barium titanate, Wul developed high-quality piezoelectrics which in many respects are better than quartz crystals and Rochelle salt.

The use of piezoelectrics in acoustic defect detectors, adapters, loud-speakers, and in radio broadcasting will improve considerably the quality and intensity of the sound.

7. RECTIFIERS OF ALTERNATING CURRENT AND AMPLIFIERS OF RADIO OSCILLATIONS (TRANSISTORS)

Semi-conductors entered the field of radio at the end of the 1920's in the form of solid rectifiers of alternating current first on the basis of cuprous oxide, then selenium and cuprous sulphide, and later silicon and germanium.

The first copper-oxide rectifiers were made of copper plates, on which a layer of cuprous oxide (Cu_2O) was deposited at a temperature of approximately $1,060^\circ\text{C}$.; this layer was then saturated with additional oxygen at 600°C . and subjected to rapid cooling. The upper layer of copper oxide (CuO) which appeared on such a plate was removed by dissolving in acid. Then metallic copper was applied to the uncovered cuprous oxide.

In a plate prepared in this way, there appears a thin layer on the junction between the initial copper and the cuprous oxide. The resistance of this layer to a current directed from the cuprous oxide to the copper is thousands of times smaller than in the reverse direction. It is called a barrier layer; the direction of the current is first forward and then reverse.

We shall try to answer the following two questions: 1) why does the barrier layer (despite its negligible thickness of a fraction of a micron) concentrate within itself the principal part of the resistance? If this were not the case, the remaining part of the layer of cuprous oxide together with the resistance, which does not depend on the direction of the current, would nullify the effect of the barrier layer; 2) why does the resistance of the barrier layer vary with the direction, and precisely as we have stated?

The correct answer to the first question was given by the Soviet physicist Boris Iosifovich Davydov, the German physicist Schottky and the English physicist Mott.

Cuprous oxide is a semi-conductor with hole conduction; a part of the electrons pass from the filled band to the ex-

cess atoms of oxygen present in the oxide, thereby releasing in this region more holes; the greater the excess of oxygen in the oxide and the higher its temperature, the more holes are released.

The copper adjacent to the oxide has the same type of holes, but their connection with the medium differs: holes are better retained by copper, than by the oxide. For this reason they pass from the oxide to the copper and charge

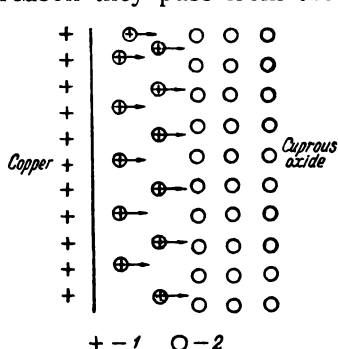


Fig. 12.

Junction of metallic copper and cuprous oxide.

1—positive charges; 2—Holes.

it with positive electricity, leaving in the oxide a negative layer with a small number of holes. The transition of charges continues until the holes are repulsed by the positive charge of the metal, thereby equalizing the tendency of the holes to reduce their energy by passing into the copper. The repulsion of the holes by the positive charge of the copper extends a certain distance into the cuprous oxide near its junction with the copper, forming here a layer with a reduced con-

centration of holes, and therefore with reduced electric conductivity (fig. 12).

From this explanation it follows that on the boundary between this same cuprous oxide and the metal, which has a weaker hold on the holes than the oxide, the holes ought to strive to pass from the metal into the oxide and produce there a positively charged layer with an excess of holes and a high conductivity, whereas on the surface of the copper the holes should tend to create a negative charge that attracts the holes of the oxide to the junction. Vadim Evgenyevich Lashkarev called this layer an anti-barrier layer.

If we were dealing not with a *p*-type but with an *n*-type

semi-conductor, for example titania, the same explanation could be applied to the transition of free electrons. We would then arrive at the conclusion that on the junction of such a metal, which takes a firmer hold on the free electrons than a semi-conductor, there is formed a layer depleted of electrons and with reduced conductivity, whereas at the same junction of a metal that does not attract its electrons so strongly, an anti-barrier layer of increased conductivity is formed.

The above conclusions were fully confirmed for a large number of different semi-conductors and metals by Anna Vasilyevna Yoffe; the work required to dislodge an electron from a given body was used by her to judge the strength of the bond between the electrons or holes and the medium.

If two bodies are brought into contact, electrons will pass from one into the other until they are so charged as to stop any further movement. A difference of potential, which is called contact potential, will be established between them. A. V. Yoffe confirmed the correctness of Davydov's theory by measuring the contact potential differences of a number of metals and semi-conductors.

B. I. Davydov, Schottky and Mott also showed that the resistance of the barrier layer varies with the direction of the current: when the external electric field acts in the same direction as the field produced by the charge on the surface of the metal, the resistance increases still more; however, when the external field counteracts the charge of the metal, the resistance of the layer decreases. This is the forward direction of the current.

Though A. V. Yoffe's experiments also confirmed this conclusion of Davydov, the relation that she observed between the opposite currents never reached the values observed in technical rectifiers. The forward current did not exceed the reverse current by more than several dozen per cent and only rarely reached two or three times, whereas in solid rectifiers the ratio between the currents was in the thousands. On the other hand, A. V. Yoffe obtained a recti-

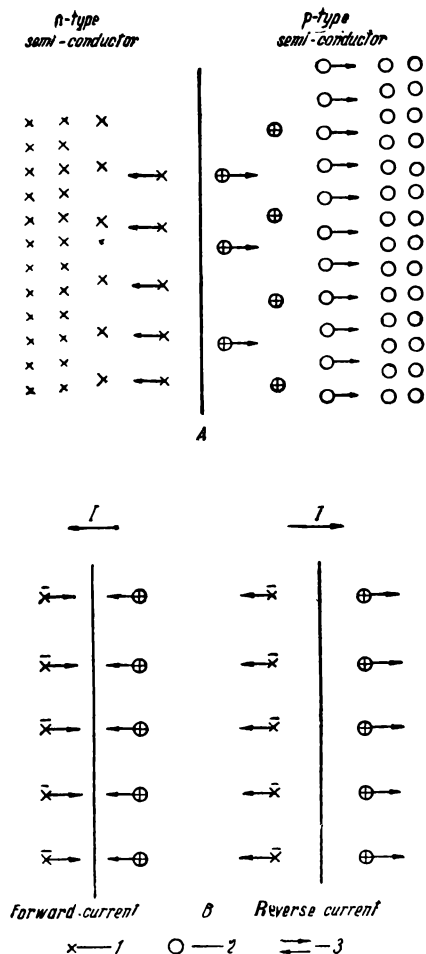


Fig. 13.

A—Junction of *p*-type semiconductor and *n*-type semiconductor;

B—Forward and reverse currents.

1—Electrons; 2—Holes; 3—Velocities.

fication of the order of 10,000 and more at the junction of *p*-type and *n*-type semiconductors, for example, cuprous oxide (Cu_2O) and titania (TiO_2). It was natural to assume that technical rectifiers also had such a junction. In a given direction of the current the holes in one semiconductor and the electrons in the other move toward each other creating a forward current; when the current is reversed they move in the opposite direction, thus increasing the resistance of the non-conducting barrier layer (fig. 13B).

In copper-oxide rectifiers, cuprous oxide is bounded on both sides by copper, and it would seem that when the current is in either direction, one or the other junction would be connected in the blocking direction, i.e., so that the positive holes proceed from the metal into the semiconductor. But one of the copper electrodes has a layer of oxide formed by

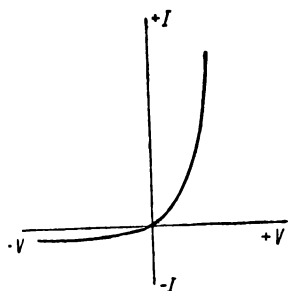


Fig. 14.

$+I$ —Forward current; $-I$ —
Reverse current.

oxidation of the copper, i.e., a layer of cuprous oxide having an excess of copper and other impurity metals that easily give up their electrons; on the other hand, the copper borders on the oxide that was saturated at 600°C . with excess oxygen which forms holes. It might be expected that at the first junction, the excess copper in the oxide created a layer with electronic conduction and that the p -type oxide is

thus adjacent not to the copper, but to the n -type cuprous oxide. This is what creates the strong rectification here. But on the other side, there is a junction with the copper that does not produce noticeable rectification.

V. E. Lashkarev actually succeeded in observing directly a thin layer of cuprous oxide with electronic conduction at the first junction.

A correct theory of rectification at the junction of two semi-conductors with opposite-sign current carriers was developed on this basis by B. I. Davydov, and it was later worked out in detail by Alexander Ivanovich Gubanov.

Another and now most widely used type of solid rectifier is the selenium rectifier which consists of a nicked iron plate with an applied layer of selenium, on which is then applied a layer of an alloy of cadmium, tin and bismuth. The rectifier is formed after continued heating and passage of current.

Like in cuprous oxide, the conduction in selenium is of the hole type. Rectification takes place here not at the junction of the selenium and the metal, but at the junction of the cadmium selenide that was formed during manufacture and that possesses electronic conduction.

The dependence of the intensity of the current I , that

passes through the rectifier, upon the potential difference V applied to it, is shown in fig. 14. It may be seen that the forward current increases rapidly with the voltage whereas the reverse current is small and hardly increases at all.

In the post-war years, germanium and silicon rectifiers have found broad practical application. By introducing the appropriate impurities it is also possible to form a region of p -type semi-conductor transition or, as it is called, a p - n junction.

In certain semi-conductors, such as silicon, germanium, lead sulphide and others, the introduction of one type of impurity produces electronic conduction, and that of another type, hole conduction. If the primary material has been carefully purified, even minute proportions of impurity atoms (a thousandth part or even a millionth part of one per cent) are sufficient to change the type of conduction. It is possible, by treating germanium or by diffusion from an electrode, to produce a thin layer of p -type germanium on the surface of n -type germanium, thus making rectification possible.

When radio was just beginning to develop, amateurs used crystal detectors of radio waves (Oleg Vladimirovich Losev even succeeded in producing a generator of radio oscillations). Sensitive spots were found on the surface of the semi-conducting crystal, and a metal point applied to such a spot was found to have rectifying properties: high-frequency alternating currents caused by the radio waves met a high, reverse resistance in one direction and a low resistance in the other direction. The uni-directional currents obtained were easily detected in earphones.

The sensitive regions were presumably those where a p -layer bordered on an n -layer, and the point produced good rectification since the principal part of the crystal resistance was located in the thin junction layer that surrounded the point, in which layer the rectification was concentrated. The additional resistance of the remaining part of the crystal,

which does not depend on the direction, did not play a marked role.

However, the detectors of radio amateurs did not provide stable operation, and the finding of sensitive spots was a matter of chance. Compared to these detectors, the germanium and silicon detectors which were introduced during World War II are stable in operation, and the transition from the n -layer to the p -layer is produced at will; the metallic electrode is firmly welded to the semi-conductor. The negligible capacity of such point detectors and their small size have made it possible to use them in radar for even the shortest centimetre waves. The outstanding advantages of semi-conductor rectifying devices as compared with vacuum valves are: absence of preliminary heating of a filament that is necessary in vacuum electron valves, insensibility to mechanical shock, simplicity of manufacture and, connected therewith, the possibility of mass production.

It was soon found possible to use germanium and silicon not only for rectification but also for amplifying radio oscillations. By placing on the surface of germanium (provided with a common base electrode) two closely spaced points, of which one is connected in the forward direction, and the other in the reverse direction, it proved possible to transfer to the barrier layer (which is non-conducting due to the nearly total absence of free charges) current carriers from the adjacent sector, which is rich in charges and connected in the forward direction. A particularly big effect is produced by the injection of holes into an n -layer and vice versa.

The currents amplified or rectified by point electrodes are small.

More powerful amplifiers and rectifiers are made not with point electrodes but with large junctions between n -type and p -type semi-conducting material. They are also made of a single germanium crystal, in which either a thin p -type layer is between two larger layers of n -type semi-conductor or vice versa, an n -type layer between two p -type layers. The free charges pass through the thin layer from the better

conducting section (on one side) into the barrier layer on the other side. *P-n* junctions and layers in single crystals are made by introducing the appropriate impurities during crystallization. Such junction amplifiers have considerably greater capacitance than those of the point-contact type and cannot be used for centimetre waves, but in the range of long waves and sound frequencies they have distinct advantages over radio valves.

Germanium rectifiers with artificially produced *p-n* junctions have great advantages in rectifying ordinary alternating current. Whereas in copper-oxide rectifiers the power of the direct current does not exceed 70 to 75 per cent of the alternating current power, and in selenium rectifiers the efficiency is of the order of 80 per cent, in germanium rectifiers it exceeds 95 per cent, and the current density is many times greater than the current densities permissible in selenium and copper-oxide rectifiers.

Semi-conductor devices came into being only a few years ago, but they are already widespread. They are being rapidly improved, their field of application is growing, and for certain purposes they have replaced the older devices. Their introduction into the radio industry signifies a new stage in the development of radio engineering, a stage not less significant than the appearance of electron vacuum valves at the end of the first decade of this century.

8. PHOTOCELLS

Semi-conductor photoconductive cells detect and measure radiant energy by the variation of current intensity produced by an external electromotive force. Photocells appeared at the end of the 1920's. They are devices that create electric current from the energy of light, dispensing with external sources of energy. This became possible through the use of barrier layers, which, as we have seen, form in a semi-conductor at the junction with an appropriate electrode.

It is possible to deposit on the surface of a semi-conductor such a thin layer of metal (gold, for example) that light will pass through it into the semi-conductor. The light, by conveying to the electrons its energy, liberates them and creates conditions for their transition through the barrier layer into the metallic electrode. The flow of electrons creates a potential difference between the electrode and the semi-conductor, which is separated from the former by a non-conducting barrier layer. This difference of potential generates electric energy in a closed circuit when the photocell is illuminated. Obviously, the frequency of the light must, in this case, exceed ν_{min} , i.e., the minimum frequency required to transfer an electron inside the semi-conductor into the free state.

The first photocells were made of cuprous oxide, later selenium was used. Selenium photocells are still used since their spectral sensitivity is close to that of the human eye, thus making it possible to describe the illumination perceived by the eye.

In copper-oxide photocells, as in rectifiers, the barrier layer is situated at the junction of the copper and the oxide. If the external electrode in a copper-oxide photocell is transparent, but does not create a barrier layer, then the photocell will register only the light that has passed through the transparent electrode and the whole layer of oxide; and red is the only light that does; light of a higher frequency or shorter wave length is totally absorbed. But copper-oxide photocells, in which a barrier layer has been artificially formed under the external transparent electrode, are sensitive both to the yellow and green parts of the spectrum.

The electromotive forces that arise when a strong light strikes such photocells, approach one volt, and the current intensity is several hundred microamperes per lumen of light (a lumen is defined as the quantity of light received upon a surface of one square metre at a distance of one metre from the source with an intensity of one candle).

The Soviet physicists Yury Petrovich Maslakovets and Boris Timofeyevich Kolomiets designed a far more sensitive

photocell made of thallic sulphide; it has a sensitivity of up to 10,000 microamperes per lumen. D. S. Heikhsman, of the Institute of Physics of the Ukrainian Academy of Sciences in Kiev, developed a similar photocell made of silver sulphide, which was later improved by V. E. Lashkarev.

Photocells may be regarded as devices that convert luminous energy into electric energy. Their efficiency, however, is low. The ratio of electric energy produced in a photocell made of cuprous oxide or selenium to the incident luminous energy does not exceed several hundredths of one per cent. This ratio reaches one per cent in photocells made of thallic sulphide or silver sulphide.

Silicon and germanium photocells with $p-n$ junctions and a considerably higher efficiency of the order of 10 per cent have recently appeared. Improved technology in their manufacture may so cut their cost as to make it profitable to convert the energy of the sun's light into electric power. It may be recalled that the efficiency of plants in utilizing light when converting a part of the solar energy into fuel energy does not even reach 1 per cent. Incidentally, it may be expected that the photochemical utilization of the sun's energy, which in a successful solution of the problem may have an efficiency approaching 100 per cent, will prove more profitable than the use of photocells.

Nevertheless, it is evident that for purposes of automation, signalization, remote control, and possibly in sound motion pictures, semi-conducting photocells have great advantages in that they do not require any outside source of current.

The concentration of electrons or holes near the $p-n$ junction may be raised not only by light, but also by the rays of radioactive substances applied to the surface of the semiconductor. In this case, electric energy is obtained from nuclear energy.

Chapter III

THE HISTORY AND FUTURE OF SEMI-CONDUCTOR THEORY

The theory of the properties of semi-conductors developed in close contact with their technical applications. As more new applications were found, the theory developed and new types of materials were investigated.

The photoelectric properties of selenium were already known at the end of the 19th century. At the beginning of the 20th century selenium photoconducting cells were used as a basis for a system of picture transmission over wires. Hundreds of scientific investigations were devoted to selenium, and since the time selenium photocells with barrier layers appeared together with the industry of selenium rectifiers, the number of works devoted to selenium has passed the 1,000 mark. And still the mechanism of conduction and photoconduction of selenium is not yet understood.

The first solid rectifiers of alternating current were developed in the 1920's. These were followed by photocells made of cuprous oxide. Since that time cuprous oxide was for many years the basic material used to investigate and verify semi-conductor theory. There are hundreds of works devoted to the investigation of the properties of cuprous oxide. This research did much to improve the technology and quality of rectifiers, it explained the mechanism of rectification and a number of other phenomena that are observed at the point of contact between semi-conductors and electrodes. The

rectification theories of B. I. Davydov, D. I. Blokhintsev, S. I. Pekar and A. I. Gubanov appeared; and A. V. Yoffe's experiments devoted to a study of junctions between semi-conductors and metals and between p -type and n -type semi-conductors were announced. During the war (1941-45), radar requirements in the U.S.A. called for rectifiers and amplifiers of high-frequency currents. These were developed on the basis of silicon and germanium, where use was made of the properties of junctions of p -type and n -type silicon or germanium.

Since that time, germanium has become the chief object of scientific investigation. During the past 10 years, extensive researches have been published explaining the mechanism of the p - n junction. These papers have brought to light a large number of new facts and have further developed both semi-conductor theory and the general theory of solids. At present, it is germanium and its properties that have been most thoroughly investigated and are best understood.

The interest of research workers is turning from germanium to other semi-conductors similar to germanium: studies have been made of diamond, graphite, silicon and a gray modification of tin, the crystal lattice of which is similar to that of germanium; investigations are being conducted on compounds of related elements (aluminium, gallium, indium, phosphorus, arsenic and antimony) having a similar lattice, in the hope of finding a substitute for germanium and of further developing the applications of semi-conductors in the field of radio engineering.

The use of the photoelectric properties of semi-conductors directed the interest of researchers to materials that possess exceptional photoelectric properties.

Thallic sulphide began to be used for sensitive photoconducting cells, and recently cadmium sulphide also. These were followed by photocells with barrier layers made of thallic sulphide and silver sulphide. Devices where p - n junctions in silicon, germanium and other similar materials are used to obtain electric energy from luminous energy of radioac-

tive radiations, should be of still greater importance. A thorough study of these materials, which are used in radio engineering as detectors and amplifiers, led to the possibility of making such devices.

The demand for sensitive instruments to detect infrared radiation led to a series of studies of selenide and telluride and sulphur compounds of lead, bismuth, and tin. Photoelectricity served as a basis for the development of the theory of the optical properties of semi-conductors, for Y. I. Frenkel's theory of excitons, and for the investigations of E. F. Gross.

Problems connected with the use of luminophors created a special branch of knowledge with its own technology and terminology and its broad range of fluorescent and phosphorescent materials, both organic and non-organic (zinc sulphide). We are indebted to the school of S. I. Vavilov for the development of the theory of luminescence.

The oxides of copper, uranium, titanium and other elements are those most extensively used for thermistors, in close connection with which there developed the theory of the mobility of electrons and holes, the temperature dependence of electric conductivity, and the annealing and hardening of semi-conductor compounds.

Alumina has been studied in detail because of its use in electrolytic condensers in radio.

The use of oxide cathodes in vacuum engineering led to an investigation of the properties of a number of oxides at temperatures above 1,000°C. and to the study of diffusion in solids at high temperatures.

The ties that connect scientific research and industry are of a decidedly mutual character. New production processes are time and again built up on the basis of a scientific discovery of a new property in semi-conductors. On the other hand, the production process not only stimulates scientific research but also poses new problems, the solution of which advances semi-conductor theory. It is hard to name another branch of knowledge in which theory and practice during

the past 25 years have been so mutually beneficial and interpenetrating as semi-conductors, in the development of which Soviet physicists and engineers have played a big part.

The above-mentioned applications of semi-conductors do not exhaust their role in the national economy. We need only recall, for example, that the majority of catalysts in chemical reactions are semi-conductors, and that a study of the mechanism and effectiveness of catalysts is closely related to the study of the properties of semi-conductors.

During recent years, attention in solid-state physics has been concentrating on semi-conductors. The study of the electric, thermal, and optical properties of insulators and metals is also developing on the basis of experience gained in the investigation of semi-conductors. Metals and dielectrics are regarded as extreme cases of semi-conductors, and a better understanding of their properties is gained through a study of the central object of investigation, i.e., semi-conductors.

The first theory of semi-conductors was taken totally from the earlier formulated (1928) quantum theory of metals proposed in one of its forms by Y. I. Frenkel, and in another, simultaneously, by Sommerfeld. Later, however, metals and semi-conductors exchanged places; the study of semi-conductors became the source of new ideas in solid state physics.

Throughout the whole history of the development of semi-conductor theory, the quantum theory was a reliable guide to an understanding of the physical nature of the phenomena under investigation.

However, accumulating experimental and industrial data showed up weak spots and a certain incompleteness in the theory, which at times was even in conflict with experiment.

Thus, the theory of thermoelectromotive forces leads to the conclusion of their growth with lowering temperature, whereas in actuality these forces fall with the temperature. Their magnitude and temperature variation are frequently at variance with experimental evidence.

The analogy between the movement of electrons in a semi-conductor and that of gas molecules, which proceeds from the conception of long straight paths of the electrons, carries no weight in the case of substances where the path length is less than the interatomic distance, as is the case with certain semi-conductors with low mobility. While in semi-conductors the concepts of electronic and hole conduction have a clear physical meaning, in the case of metals no concrete model can be provided for hole current.

The quantum theory of semi-conductors builds its conceptions on a postulated perfect periodic crystal lattice in the semi-conductor. But Anatoly Robertovich Regel and his collaborators showed that melted semi-conductors, in which there cannot be any crystal lattice, have the same properties. Regel proved in a number of cases that the properties of semi-conductors are determined not by the periodicity of the crystal but by the type of chemical bond between the atom and its immediate neighbours. These facts have not yet been interpreted theoretically.

The pressure of new facts and the demands of industry perfect and develop semi-conductor theory and help to eliminate its shortcomings.

The semi-conductor industry has developed still more rapidly. Thirty years ago semi-conductors did not exist either in the electric industry or in radio engineering. At present, alternating-current rectifiers, semi-conductor detectors and high-frequency amplifiers occupy a prominent place in industry. Semi-conductors serve as a basis for automation, signalization, and remote control. Daylight lamps are gaining general recognition. High-frequency condensers made of alumina and barium titanates and also ferrite transformer cores are being produced on a large scale. Semi-conductor thermocouples are also finding applications.

A very intriguing future has been opened up by this first step in the industrial use of semi-conductors. Foreseeable is the solution by semi-conductors of such fundamental problems as the direct conversion of thermal energy and the

solar energy into electric power, and also electric energy into mechanical energy, and vice versa, without machines and also such problems as thermo-dynamically profitable heating and the production of cold by electric current, the concentration of high-frequency electric and magnetic energy, night lighting with stored daylight, cheap lighting for each particular purpose, such as the growing of plants, and the like. The highest quality radio receivers and the most intricate apparatus for signalization, automation and remote control will be tiny in size and will cost a fraction of what they do now. The radioactive radiations of nuclear reactions will become a source of electric power.

When considering the future development of semi-conductor theory, we must keep in mind that it is one of the youngest branches of science, being of the same age as nuclear physics, to which it is an immediate second in importance and rate of development.

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